1967

Electronic Structure and Geometry of 2-Phenylnaphthaleme Derivatives. A Study of the Electronic Transitions Observed in Absorption, Fluorescence and Phosphorescence Spectra.

Homer Edward Holloway
Louisiana State University and Agricultural & Mechanical College

67-13,990

HOLLOWAY, Homer Edward, 1933-

ELECTRONIC STRUCTURE AND GEOMETRY OF 2-PHENYLNAPHTHALENE DERIVATIVES. A STUDY OF THE ELECTRONIC TRANSITIONS OBSERVED IN ABSORPTION, FLUORESCENCE AND PHOSPHORESCENCE SPECTRA.

Louisiana State University and Agricultural and Mechanical College, Ph.D., 1967
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

ELECTRONIC STRUCTURE AND GEOMETRY OF 2-PHENYLNAPHTHALENE DERIVATIVES. A STUDY OF THE ELECTRONIC TRANSITIONS OBSERVED IN ABSORPTION, FLUORESCENCE AND PHOSPHORESCENCE SPECTRA

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Homer Edward Holloway
B.S., University of Akron, 1957
May 1967

ACKNOWLEDGMENT

This research was suggested by Dr. R. V. Nauman and was carried out partly under his direction and partly under the direction of Dr. James H. Wharton during Dr. Nauman's sabbatical leave. The guidance and untiring efforts of both were indispensable to the success of this research. Appreciation is expressed to the National Science Foundation for a Science Faculty Fellowship, which made this research possible.

The writer wishes to express appreciation to Dr. D. H. Hey and Dr. Milton Orchin, who kindly donated compounds for this research, and to Dr. J. G. Traynham and Dr. Eugene W. Berg for their helpful advice concerning preparation and purification of compounds.

Many fellow graduate students generously contributed their time and effort. In particular the writter wishes to express appreciation to J. R. McDonald for his help in setting up experimental apparatus, to Kenneth P. Reed and Jaime Chiang for assistance in compound purification and to Brent J. Bertus for computer calculations.

The writer gratefully acknowledges financial assistance from the Dr. Charles E. Coates Memorial Fund of the L.S.U. Foundation

donated by George H. Coates for expenses pertinent to the publication of the doctoral dissertation.

The writer is also deeply indebted to his wife for her understanding and patience throughout the research and preparation of this manuscript.

TABLE OF CONTENTS

TABLE OF CONTENTS (Contd.)

LIST OF TABLES

LIST OF TABLES (Contd.)

LIST OF TABLES (Contd.)

LIST OF FIGURES

LIST OF FIGURES (Contd.)

LIST OF FIGURES (Contd.)

ABSTRACT

The dual emissions previously reported for fluoranthene, 2-phenylnaphthalene and 1,2-benzfluorene have been shown to originate from traces of impurities present in these compounds and are not characteristic of the subsystems of the molecules themselves.

The electronic states of 2-phenylnaphthalene have been evaluated as a function of the angle between the aromatic rings by means of spectroscopic studies on the 1-halo, 6-bromo, 2'-halo, 4'-halo and 2'-methyl derivatives of 2-phenylnaphthalene. The electronic states of planar 2-phenylnaphthalene are compared with those of 1,2-benzfluorene. The room temperature solution absorption spectra and the 77°K absorption, fluorescence and phosphorescence spectra from rigid glassy solution are shown for all the 2-phenylnaphthalene derivatives that were studied.

Experimental evidence is presented to indicate that strong coupling exists between the two rings of 2-phenylnaphthalene in the ground state and that the interaction energy increases in the excited state. There is strong evidence for a rotation from an out of plane Franck-Condon excited state to a planar equilibrium excited state. The ring coupling is minimized as the angle between the rings approaches

90 degrees. There is some indication of stabilization of the 90 degree configuration in some of the halogen derivatives by halogen-pi cloud interactions.

Evidence is presented which indicates that even the most weakly coupled 2-phenylnaphthalene configuration cannot exhibit emission properties characteristic of both the benzene and naphthalene subsystems. If two emissions were to be observed from 2-phenylnaphthalene, they would originate from two different molecular configurations. All the assignments of the energy states observed in 2-phenylnaphthalene are those of the total molecule. SCFMO calculations of these energy states were carried out on the planar 2-phenylnaphthalene system using the methods of Pariser, Parr and Pople. The results of this computation agree well with the experimental data.

Fluorescence and phosphorescence quantum yields and phosphorescence lifetime data are presented for all compounds that were studied. The spin-orbital coupling effects for halogen substitution in the phenyl ring tend to indicate that there is very strong coupling between the subsystems in the triplet state. The emitting species in the triplet state is also attributed to a total molecule chromophore.

CHAPTER I

LITERATURE SURVEY AND THEORY

A. Introduction and General Theory

The electronic states of several composite molecules composed of smaller interacting subsystems have recently been interpreted in terms of the electronic states of the subsystems. Molecules of this type that have received the most attention both experimentally and theoretically are fluoranthene, the phenylnaphthalenes, and the benzfluorenes. All these compounds are composed of individual benzene and naphthalene subsystems. The fluoranthene system was studied by Ory[1] and Wharton.[2] The data were interpreted by Wharton in terms of exciton interaction theory. Both the theoretical and the experimental studies seemed to indicate that the molecules had electronic states characteristic of both the benzene and naphthalene subsystems. The 2-phenylnaphthalene system was studied by Harris[3] who concluded from experimental data that there were electronic states characteristic of a total molecule and those characteristic

---

[1] Horace Ory, Ph.D. Dissertation, Louisiana State University, Baton Rouge, (1957), p. 41.

[2] J. H. Wharton, Ph.D. Dissertation, Louisiana State University, Baton Rouge, (1962), p. 1-4.

[3] J. Harris, Ph.D. Dissertation, Louisiana State University, Baton Rouge, (1965), p. 39.

of the naphthalene subsystem. Dual fluorescences and phosphorescences were reported in all these investigations. In general there is observed only a single fluorescence and phosphorescence emission from a single molecular species for molecules having normal energy level spacings. This investigation was initiated to further characterize the electronic states and dual emission properties of 2-phenylnaphthalene and to determine definitely whether or not these emissions arise from the individual subsystems.

In order to interpret the composite molecules as "molecules within molecules", it is necessary to consider the different cases that may arise when the coupling between the subsystems varies from no interaction at all to some large value in which the subsystems lose their individual identities. The simplest situation that can arise is the hypothetical case in which the subsystems are completely independent. In such a system the spectroscopic properties of the molecule should be exactly those of the combined independent subsystems. These properties should be exactly the same as those of a physical mixture of the molecular species comprising the subsystems. The absorption spectrum of molecules of this kind should be a superposition of the absorption spectra of the individual subsystems. The fluorescence and phosphorescence emissions of both subsystems should be observable when properly excited under conditions that minimize intramolecular energy transfer. If the absorption transitions of the two subsystems are sufficiently separated so that only subsystem 1 is excited, only the emission characteristic of subsystem 1 would be observed and if

subsystem 2 were excited, only the emission characteristic of subsystem 2 would be observed. In the case of weakly coupled molecules in which aromatic subsystems are insulated from each other by methylene groups, the vibrational frequencies of the first excited state have been observed to be those characteristic of the individual aromatic rings. This conservation of vibrational frequencies, however, does not occur when the rings are strongly coupled through groups such as -CH = CH-.[4]

In most real molecular systems, there will be some coupling between the individual subsystems, even though this coupling may be very small in some cases. In such weakly coupled systems, one may still observe the properties of the individual subsystems but the properties of a given subsystem may be somewhat perturbed by the presence of the second subsystem.

Since in this work molecules containing two different subsystems are being considered, the problem of energy transfer between the coupled subsystems must also be considered. The term energy transfer is usually reserved for the non-radiative transfer of excitation energy from one excited donor species to another acceptor species the lowest excited state of which has lower energy than that of the donor. The mechanism for this radiationless transfer between molecules has been treated by Förster[5] and has been applied to other systems,[6]

---

[4] D. S. McClure, Solid State Physics, 8, (1959), p. 3.

[5] Th. Förster, Fluoreszenz Organischer Verbindungen, Vanderhoek and Ruprecht, Goettingen, (1951), Chapter IV.

[6] Th Förster, Disc. Faraday Soc. 27, (1959), p. 7.

in which the transfer occurs between two interacting subsystems such as those studied in this research. Consider how this process may occur in a system like 2-phenylnaphthalene. In this system the benzene portion of the molecule must be the donor species. Assume the benzene subsystem to be excited to its first excited singlet state. In a very short interval of time, 10^{-13} - 10^{-12} sec., it is internally converted to the lowest vibrational level of that state. Assuming that the temperature is low enough, the excited species will remain at this lowest vibrational level throughout the remainder of its electronic lifetime of about 10^{-6} sec. After this time interval it will return to the ground state by a spontaneous radiative or non-radiative process. Suppose that the energy difference for one of these possible deactivating processes in the donor species corresponds exactly to that for a possible absorption transition in the nearby acceptor species, the naphthalene subsystem in this case. Then with sufficient energetic coupling between these species, both processes may occur simultaneously, resulting in a transfer of excitation from donor to acceptor. The conditions favorable for this resonance transfer are sufficient overlap between the donor fluorescence and acceptor absorption and a sufficiently short distance between donor and acceptor species. Both these conditions are very adequately met in the subsystems of 2-phenylnaphthalene. The fluorescence spectra of benzene derivatives almost identically coincide with the relatively intense $^1L_a \leftarrow {}^1A$ absorption transition of naphthalene. Since the two subsystems are separated by only approximately 1.5 A., the conditions are very favorable for resonance energy transfer.

The rate of energy transfer between two molecules or two "molecules within a molecule" depends on the magnitude of the coupling between the donor and acceptor species. If the rate of energy transfer is extremely slow, it would be possible to observe the emission properties of the benzene subsystem before the excitation energy is transferred to the naphthalene portion of the molecule. There exists some amount of coupling between the two subsystems, above which the rate of energy transfer becomes too rapid to observe the individual emission properties of the benzene subsystem. This, for all practical purposes, must occur at the point at which physical measurements are no longer capable of observing these individual properties. It is difficult to evaluate this interaction energy. However, it can be estimated for typical organic molecules on the basis of the uncertainty principle, which may be written in the following form:[7]

$$\tau = \frac{h}{\Delta E} \quad , \tag{1}$$

in which τ is the average time that the excitation energy remains on the donor subsystem before it is transferred to the acceptor, h is Planck's constant and ΔE is the interaction energy between the donor and acceptor. This equation was applied by McClure in cases where electronic and vibrational interactions were evident. In that particular case the value of ΔE included the vibrational and electronic coupling (interaction energy) between the subsystems of the

---

[7] D. S. McClure, loc. cit.

double molecules. The value of ΔE was determined from splittings in the vibrational bands of the double molecules as compared with those of the individual subsystems.

If electronic excitation in 2-phenylnaphthalene is localized in the subsystems, the electronic energy transfer rate between subsystems is of primary interest. In the case of 2-phenylnaphthalene the magnitude of ΔE for each transition should be determined for the most part by the electronic coupling between the two subsystems. Thus ΔE for each transition could be estimated from the shifts observed in the individual absorption bands of 2-phenylnaphthalene compared with those of the individual subsystems. Whether or not an emission from the assumed phenyl subsystem would be observed depends upon the electronic coupling between the transition to the lowest energy state of the phenyl subsystem and the lower energy transitions in the naphthalene subsystem. This means that shifts observed in the $^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ transitions of 2-phenylnaphthalene compared to those of naphthalene should reflect the ΔE of interaction pertinent to the rate of energy transfer. It is also possible for the donor species to transfer energy to the surrounding molecules; however, coupling with a subsystem of the same molecule will nearly always be greater than that with other molecules, hence the intramolecular transfer will be the limiting factor.

If the value of τ is not greater than one vibrational period for a particular part of a molecule, it is of no value to even consider that part as being an independent subsystem. In such a situation there is no basis for identification of the vibrational frequencies

as belonging to a given subsystem. Since vibrational periods are of the order of 10^{-10} - 10^{-13} sec., this corresponds to an interaction energy of 0.3 - 300 cm.$^{-1}$. These energy differences are on the borderline of being too small to be measurable from ultraviolet spectra.

If one takes the stand that the separate energy states of the independent subsystems do exist, then emissions from both subsystems can only be observed if the radiative lifetime of the donor excited state is less than the time required for energy transfer to the acceptor. For most organic species the excited state lifetime is of the order of 10^{-8} sec. This corresponds to a value of .003 cm.$^{-1}$ for ΔE. In terms of 2-phenylnaphthalene, this means that if the benzene and naphthalene subsystems are coupled by an energy greater than about .003 cm.$^{-1}$, the chances of observing a benzene emission are rather remote even when the excitation is in the region of the benzene absorption.

The question of whether the properties of 2-phenylnaphthalene can be considered as being the combined properties of the benzene and naphthalene portions of the molecule has essentially been reduced to the question of whether or not the electronic interaction energy between the two subsystems is less than the 0.3 - 300 cm.$^{-1}$ limit proposed for the individual subsystems to have any vibrational identity. The question of whether or not the emissions from both subsystems can be observed reduces to the question of whether or not the interaction energy is less than about .003 cm.$^{-1}$ so that emission can successfully compete with intramolecular energy transfer.

The smallest amount of coupling will be observed in 2-phenyl-naphthalene when the two aromatic rings are at 90 degrees to each other.

Simple molecular orbital theory predicts no resonance interaction under these circumstances, because the π-electron wave functions are assumed to have a node in the plane of the molecule. This is not strictly true, however. C^{13} splittings have been observed[8] in the ESR spectrum of the naphthalene anion. If the pi orbitals had nodes in the plane of the molecule, C^{13} splitting would not be observed in the spectrum. In the opinion of the writer the interaction at 90 degrees will be much greater than .003 cm.$^{-1}$.

In order to accurately evaluate the interaction between the two rings in 2-phenylnaphthalene it is necessary to observe the changes in the electronic energy levels as the angle between the rings is varied from the planar configuration to 90 degrees out of the plane. The variation in ring angle is best accomplished by use of substituents that change the angle either by attractive forces or steric repulsions. This was the experimental approach taken by the author to evaluate the electronic energy states of 2-phenylnaphthalene.

There are three common systems for classification of electronic absorption transitions of aromatic hydrocarbons. Clar[9] has classified the bands as α, β and para according to their observed similarities in intensities and shifts with substitution along a given axis of the molecule. Platt[10] has classified the absorption bands according to

---

[8] M. Bersohn and J. C. Baird, An Introduction to Electron Paramagnetic Resonance, W. A. Benjamin, Inc., New York, (1966), p. 96.

[9] E. Clar, Spectrochim. Acta., 4, (1959), p. 116.

[10] J. R. Platt, J. Chem. Phys., 17, (1949), p. 484.

a perimeter free electron model. In this classification the α bands of Clar correspond to the $^1L_b \leftarrow {}^1A$ transition, the para bands to the $^1L_a \leftarrow {}^1A$ transition and the β bands to the $^1B_b \leftarrow {}^1A$ transition. This system designates both the ground and excited states of the transition. The third and most generally accepted classification is that based on group theory.[11] This system identifies the symmetry species of both the ground and excited states. In the 2-phenylnaphthalene molecule, the lack of symmetry makes the group theory notation somewhat unsuitable and the Clar classification has not been widely accepted in this country in recent years. The perimeter free electron model is certainly not applicable to 2-phenylnaphthalene; however, the Platt notation is used in this research on the basis of similarities of positions and intensities of the observed transitions compared with those of benzene, naphthalene and phenanthrene.

B. Kinetics of Excited State Population

Figure 1 is a schematic diagram showing the low lying excited states of a typical aromatic molecule and the rate constants for the various modes of excitation and decay. The solid lines in Figure 1 represent radiative processes and the dashed lines represent non-radiative processes. The symbols for the rate constants are identified as follows:

K_o - singlet-singlet absorption

K_F - fluorescence emission

---

[11] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys., 6, (1938), p. 645.

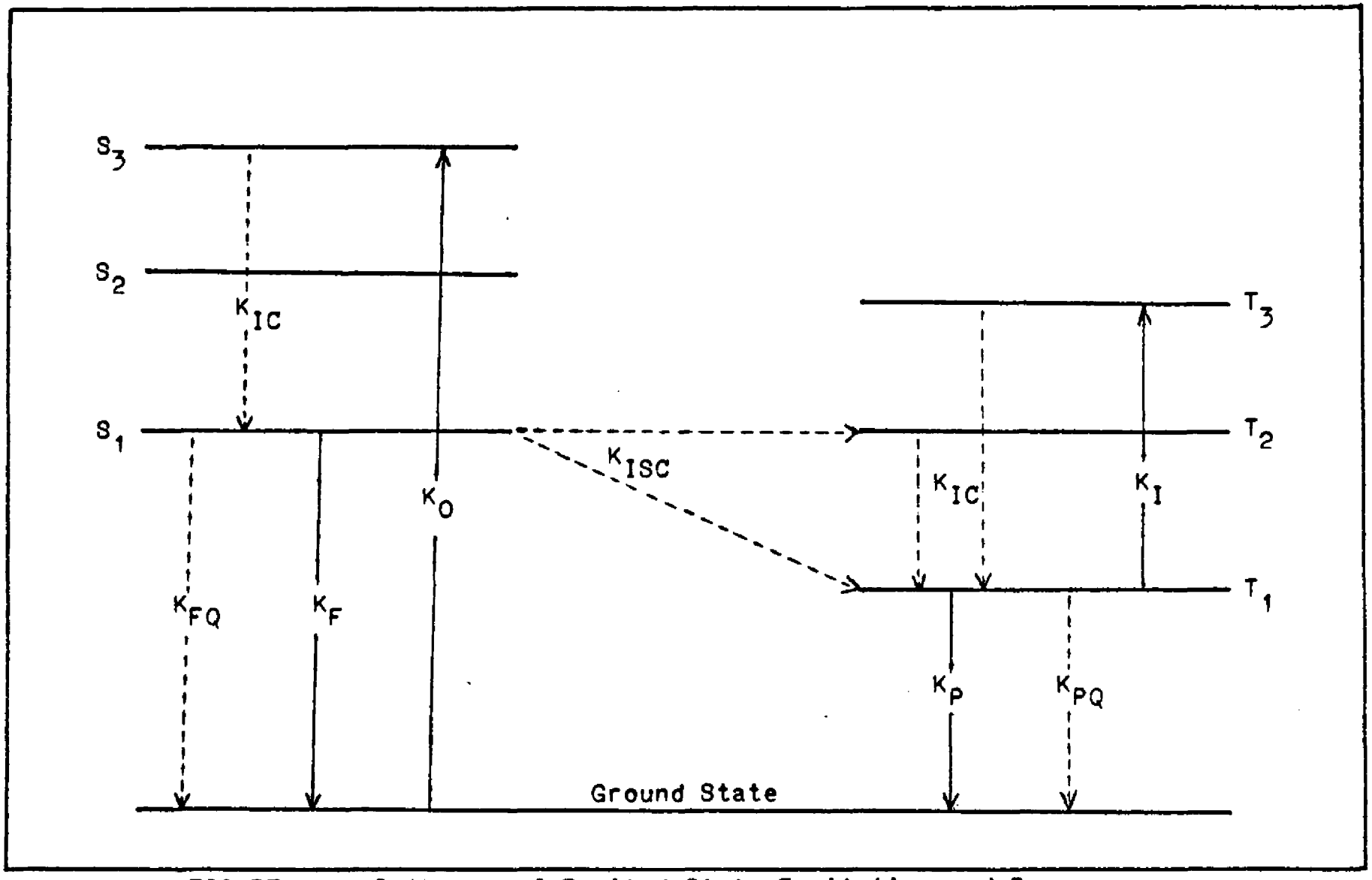


FIGURE 1. Pathways of Excited State Excitation and Decay

K_{IC} - internal conversion

K_{FQ} - fluorescence quenching (all possible modes)

K_{ISC} - intersystem crossing

K_{I} - triplet-triplet absorption

K_{P} - phosphorescence emission

K_{PQ} - phosphorescence quenching (all possible modes)

Förster[12] has discussed the kinetics of fluorescence and phosphorescence in the limiting case of low triplet concentrations and low intensity of exciting light so that triplet-triplet annihilation and triplet-triplet absorption need not be considered. The temperature will also be assumed to be low enough so that $T_1 \rightarrow S_1$ processes can be neglected. The following equations apply.

$$\text{Singlet Decay} \quad \frac{d[S]}{dt} = K_o[S_o] - (K_F + K_{FQ} + K_{ISC})[S] \tag{2}$$

$$\text{Triplet Decay} \quad \frac{d[T]}{dt} = K_{ISC}[S] - (K_p + K_{PQ})[T] \tag{3}$$

The quantum yields are given by the following equations.

$$\Phi_F = \frac{K_F}{K_F + K_{FQ} + K_{ISC}} \tag{4}$$

$$\Phi_P = \frac{K_P K_{ISC}}{\lambda} \tag{5}$$

---

[12] Th. Förster, Fluoreszenz Organisher Verbindungen, Vanderhoech and Ruprecht, Goettingen, (1951).

in which $\lambda = (K_F + K_{FQ} + K_{ISC})\ (K_P + K_{PQ})$. The observed lifetimes are given by

$$\tau_F = (K_F + K_{FQ} + K_{ISC})^{-1} \tag{6}$$

$$\tau_p = (K_P + K_{PQ})^{-1} \tag{7}$$

Since phosphorescence must compete with non-radiative decay processes that are very rapid, it is necessary to distinguish between observed phosphorescence lifetime τ_p and radiative (natural) lifetime $\tau_o = 1/K_p$, that would presumable be observed in the absence of phosphorescence quenching processes. It has been shown recently by Ermolaev and Sveshnikova[13] that all quenching in complex organic molecules at low temperatures occurs at the triplet level.

If the temperature is assumed to be sufficiently low so that $K_{FQ} = o$, the previous equations can be combined to show a simplified relationship between the quantum yield ratio Φ_P/Φ_F and the intersystem crossing rate.

$$\frac{\Phi_P}{\Phi_F} = \frac{K_P K_{ISC} \tau_P}{K_F} \tag{8}$$

Under these conditions one can define a quantum yield for phosphorescence quenching Φ_{PQ} that includes all quenching at low temperature

---

[13] V. L. Ermolaev and E. B Sveshnikova, Opt. Spectry. 16, (1964), p. 320.

so that $\Phi_F + \Phi_P + \Phi_{PQ} = 1$. It, therefore, follows that

$$\Phi_{PQ} = \frac{K_{PQ} K_{ISC}}{(K_F + K_{ISC})(K_P + K_{PQ})} \tag{9}$$

It is obvious from equation (8) that the Φ_P/Φ_F has a direct dependence on K_{ISC} but is complicated by the dependence on the other variables. K_{ISC} is not easy to evaluate in terms of the effects of any one of the other variables.

Transitions between pure singlet and pure triplet states are considered to be forbidden and this forbiddenness is justified by the orthogonality of the descriptive spin wave functions. These transitions can become allowed through mixing of the singlet and triplet states by spin-orbital coupling. Spin-orbital interaction occurs when the electrons come close to the nucleus of an atom with a large atomic number. When a heavy atom substituent such as a halogen is substituted for hydrogen in an aromatic molecule, there are observed an increase in the oscillator strength of the singlet-triplet absorption transition and a corresponding decrease in the phosphorescence lifetime. This is known as the internal heavy atom effect. There has also been observed[14,15] an external heavy-atom effect when the heavy atom is not attached to the chromophore itself but is a part of a surrounding solvent molecule. The external heavy-

---

[14] M. Kasha, J. Chem. Phys., 20, (1952), p. 71.

[15] S. P. McGlynn, Chem. Rev., 58, (1858). p. 1113.

atom effect is normally observed to be less effective than the internal heavy-atom effect. The external effect has been attributed to the formation of a charge transfer complex between the aromatic species and the solvent molecule containing the heavy atom.

There has been little work reported in the literature concerning the effect of changing the position of the heavy atom substituent. Zanker and Koerber[16] and Roy[17] have reported sensitivity of singlet-triplet absorption intensity to location of halogen substituents. These experiments have been questioned by Lower and El-Sayed[18] who think the results may have been influenced by impurities. It seems only logical that differences in spin-orbital coupling should be observed for different positions of heavy-atom substituents. This should be particularly true in a molecule like 2-phenylnaphthalene in which electronic densitities in a MO may vary considerably from one part of the molecule to another.

C. Literature Survey

Much of the experimental and theoretical work carried out on systems of "molecules within molecules" like 2-phenylnaphthalene and biphenyl involved observations and calculations of the double bond character of the "single" bond between two conjugated parts of the

---

[16] V. Zanker and W. Koerber, Z. Angew. Phys., 14, (1962), p. 43.

[17] J. Roy, Indian J. Phys., 35, (1961), p. 143,628.

[18] S. K. Lower and M. A. El-Sayed, Chem. Rev. 66, (1966), p. 223.

molecule. Pauling[19] and co-workers pointed out some years ago that when two conjugated groups are joined by a central single bond, this bond takes on some double bond character. Diffraction experiments indicate that such molecules have a planar structure when steric conditions permit coplanarity of the parts and a central bond that is shorter than that of a normal sp^2 - sp^2 sigma bond. This double bond character has been more fully treated by Coulson and Longuet-Higgins[20] who have shown, in certain simple cases, how the bond order of this central bond may be calculated by means of the method of molecular orbitals. This work was extended to many compounds, including aromatic double molecules, by Coulson and Jacobs.[21] Several conclusions were drawn from this work. It was found that increasing the size of the aromatic rings invaribly increased the bond order. This is evidenced by the bond orders of planar biphenyl, 2-phenylnaphthalene, 2, 2'-binaphthyl, and 2, 2'-bianthryl, which were calculated to be 0.370, 0.372, 0.375, and 0.380 respectively. Simpson[22,23] has applied a simple resonance force model to systems of polyenes to qualitatively account for observed alterations of bond lengths, positions of singlet-singlet absorption bands and

---

[19] L. Pauling, H. D. Springall and K J. Palmer, J. Am. Chem. Soc., 61, (1939), p. 927.

[20] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc., A195, (1948), p. 188.

[21] C. A. Coulson and J. Jacobs, J. Chem. Soc., (1959), p. 2805.

[22] W. T. Simpson, J. Am. Chem. Soc., 73, (1951), p. 5363.

[23] W. T. Simpson, J. Am. Chem. Soc., 77, (1955), p. 6164.

resonance energies. In this model the double bonds are considered to be weakly interacting subsystems of the total molecule. The method employed involves writing products of wave functions for the individual parts and taking linear combinations of these by application of perturbation theory to arrive at improved wave functions for the combined system. These wave functions in a perturbation calculation give directly a set of electronic energy levels that agree well with experiment.

The theory of exciton interaction as employed by Davydov[24] applies many of the same ideas used by Simpson. This theory considers the spectroscopic properties of a composite system of weakly interacting parts to be determined by the properties of the individual parts that have been perturbed by each other. In this theory the excitation energy is transferred back and forth between the individual subsystems and as a result the degenerate energy states are split. One of the shortcomings of exciton theory is that only limited allowance has been made for the possibility of electron transfer, which is probably very important in a system like 2-phenylnaphthalene where the two subsystems are different. Longuet-Higgins and Murrell[25] have developed a theory, which is applicable to double molecules in which allowance is made for electron transfer processes.

---

[24]A. S. Davydov, Theory of Molecular Excitons, McGraw-Hill Book Co., (1962), p. 146-160.

[25]H. C. Longuet-Higgins and J. N. Murrell, Proc. Phys. Soc. (London), A58, (1955), p. 601.

Coffman and McClure[26] have analyzed the vibrational structure of toluene, biphenyl, diphenylmethane, and dibenzyl in terms of the double molecule model. The polarized light absorption spectra of crystals of all these compounds at 20°K were determined. In all four molecules studied the spectra are produced by transitions closely related to those of benzene. In the spectra of toluene, dibenzyl and diphenylmethane, the same types of ring vibrations were observed, however, quite different types of vibrations are excited in the biphenyl transition. Some of the biphenyl vibrations were C-C stretching vibrations of the rings similar to those excited by electronic transitions in stilbene, anthracene and other conjugated aromatic molecules. Since it was possible to obtain the magnitude of the vibrational interaction between the benzene rings of these double molecules, McClure[27] attempted to correlate these values with those calculated from the double molecule model. Agreement was found to be very good for dibenzyl and diphenylmethane but was rather poor for diphenyl. These observations indicate that a double molecule approach is far too simplified for molecules like biphenyl and 2-phenylnaphthalene in which the subsystems are strongly coupled. There is an indication that a molecular orbital approach similar to those applied to conjugated aromatic molecules would be more successful.

---

[26] R. Coffman and D. S. McClure, Can. J. Chem., 36, (1958), p. 48.

[27] D. S. McClure, Can. J. Chem., 36, (1958). p. 59.

D. Molecular Orbital Calculations

The semiempirical selfconsistent molecular orbital (SCFMO) theory as formulated by Pariser and Parr[28] and Pople[29] is known to give calculated transitions energies in fairly good agreement with those obtained experimentally for both alternate and non-alternate hydrocarbons. For this reason the method was chosen to carry out the computations on planar 2-phenylnaphthalene. This computation scheme is based on the π-electron approximation with transition energies computed from π-electron wave functions obtained from configuration interaction. A summary of the approximations introduced by Pariser and Parr and Pople into the closed shell Hartree-Fock method[30] in order to make it suitable to carry out calculations on conjugated systems is given below.

The molecular orbits (Ψ_i) are taken as linear combinations of the atomic orbitals (Φ_p).

$$\Psi_i = \sum_p^N C_{ip}\Phi_p \tag{10}$$

The precise form of Φ_p is not specified. The one-electron Hartree-Fock problem for closed shell π-electron systems reduces to a matrix having elements given by the following equations.

---

[28] R. Pariser and R. G. Parr, J. Chem. Phys., 21, (1958), p. 466.

[29] J. A. Pople, Proc. Phys. Soc. (London), A68, (1955), p. 81.

[30] J. C. Slater, Quantum Theory of Molecules and Solids, 1, McGraw-Hill Co., New York, (1963).

$$F_{pq} = H^{c}_{pq} - \tfrac{1}{2} P_{pq}\gamma_{pq}, \quad p \neq q \tag{11}$$

$$F_{pp} = H^{c}_{pp} + \sum_{q} P_{pq}\gamma_{pq} - \tfrac{1}{2} P_{pp}\gamma_{pp} \tag{12}$$

P_{pq} is an element of the bond order matrix given by

$$P_{pq} = 2 \sum_{i}^{N_{occ}} C_{ip}C_{iq}, \tag{13}$$

in which the summation extends over the occupied molecular orbitals as designated by N_{occ}. The eigenvectors C_{ip} and the orbital energies E_i are determined by the secular equation

$$\sum_{p}^{N} C_{ip}F_{pq} = E_iC_{iq} \tag{14}$$

The eigenvectors used in equation (13) must also satisfy equation (14), therefore it is necessary to use some form of computer iterative procedure. Such a process provides virtual as well as occupied MO coefficients.

The following is a brief description of the assignment of semi-empirical values to the core terms H^{c}_{pq} and atomic repulsion integrals γ_{pq}. The off-diagonal elements H^{c}_{pq} in equation (11) have been treated as empirical parameters β_{pq} which have values of - 2.39 e.v. for the core where p and q are adjacent atoms contributing electrons within the aromatic rings. In the case of the 1 and 2' carbon atoms where the two rings are joined, the value of $\beta_{12'}$ = - 1.90. This value

was chosen on the basis of expected overlap from known bond lengths for similar molecules. All non-adjacent H^c_{pq} elements are neglected.

The diagonal elements may be expanded as follows

$$H^c_{pp}(i) = \int \Phi_p(i) \left| T(i) + \sum_{q \neq p} U^{nq+}_q(i) + \sum_s U_s(i) + \sum_p U^{np+}_p(i) \right| \Phi_p(i) dv \quad (15)$$

Where U^{nq+}_q represents the potential due to the core of atom q with the n electrons contributing to the π-electron system removed. U_s represents the potential due to an atom s which does not contribute π electrons to the system. T is the kinetic energy operator. The Goeppert-Mayer-Sklar approximation[31] is used for the evaluation of $(T + U^{np+}_p)$.

$$\int \Phi_p(i) \left| T(i) + U^{n+}_p(i) \right| \Phi_p(i)\ dv = E_p = -I^{(n-1)+}_p \quad (16)$$

in which $I^{(n-1)+}_p$ is the ionization potential of atom p in the appropriate valence state; the ionization potentials are taken from valence state tables of these potentials.

The core terms in the summation in equation (15) can be written in terms of a potential due to the neutral atom U^0_q and a correction term allowing for the repulsion of the π-electrons contributed by that atom. For atom q contributing n π-electrons to the system we can write equation (17).

---

[13] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys., 6, (1938), p. 645.

$$U_q^{n+}(i) = U_q^0(i) - \sum_{j \neq i}^{n} \int \frac{\Phi_q^2(j)}{r_{ij}} \, dv_{ij} \tag{17}$$

The diagonal elements then take the form given in euqation (18).

$$H_{pp}^c = i_p^{(n-1)+} - \sum_{p \neq q} (U_q^0 : pp + n_q \gamma_{pq}) - \sum_s U_s : pp \tag{18}$$

The terms $U_s : pp$ and $U_q^0 : pp$ are penetration integrals for neutral atoms that conform to the convention that

$$U_s : pp = - \int U_s(i) \, \Phi_p^2(i) dv(i) \tag{19}$$

The value of H_{pp}^c for this computation was - 11.16 e.v.

The repulsion integrals γ_{pq} are defined by equation (20).

$$\gamma_{pq} = \int \Phi_p(i) \, \Phi_p^*(i) \, \left(\frac{1}{r_{12}}\right) \Phi_q(2) \, \Phi_q^*(2) \, dv_1 dv_2 \tag{20}$$

These integrals were calculated by means of an empirical method proposed by Pariser and Parr[32] and uses data obtained from atomic spectra. For the one-center integrals the values of γ_{pp} become

---

[32] Pariser and Parr, loc. cit.

$$\gamma_{pp} = I_p - A_p = 11.08 \text{ e.v.} \tag{21}$$

in which I_p is the ionization potential of atom p in the valence state appropriate to the particular molecule under consideration and A_p is the electron affinity for the same valence state.

The method used for calculating the two-center repulsion integrals is that proposed by Mataga.[33] In this method the one-center integrals are evaluated by the method discussed previously and are used to calculate the two-center integrals by the following equations.

$$\gamma_{pq}(r) = \frac{14.397}{a_{pq} + r_{pq}} \quad \frac{ev}{A} \tag{22}$$

$$a_{pq} = \frac{28.794}{(\gamma_{pp} + \gamma_{qq})} \quad A \tag{23}$$

The final values of the repulsion integrals provided by the SCF calculations were used in the configuration interaction calculations described below.

The excited states of the molecule (Ψ_I) can be expressed as linear combinations of individual configurations Ψ_i^k in which an electron has been excited from MO Ψ_i into MO Ψ_k.

---

[33] N. Mataga and K. Nishimoto, Z. Physik. Chem. (Frankfurt, A.M.), 13, (1957), p. 140.

$$\Psi_l = \Sigma A_l^{(ik)} \Psi_i^k \tag{24}$$

The mixing coefficients $A_l^{(ik)}$ and the excitation energies are obtained by diagonalizing a configuration interaction matrix with elements given by

$$(^1\Psi_i^k|H|^1\Psi_j^\ell) = \delta_{ij}\delta_{k\ell}(E_k - E_i) + 2\langle ik|j\ell\rangle - \langle ij|k\ell\rangle \tag{25}$$

in which E_i is the orbital energy of SCFMO Ψ_i. $\langle ik|j\ell\rangle$ and $\langle ij|k\ell\rangle$ are molecular repulsion integrals defined by

$$\langle ik|j\ell\rangle = \sum_p \sum_q E_{ip}C_{kp}C_{jq}C_{\ell q}\gamma_{pq} \tag{26}$$

In this calculation 25 configurations involving excitations from the highest occupied MO's to the lowest unoccupied MO's were used.

The oscillator strengths f_l of the l_{th} excited states of energy E_l are calculated with the aid of the following equation.[34]

$$f_l = 8.753 \times 10^{-2} Q_{0\to l}^2 E_l \tag{27}$$

in which $Q_{0\to l}$ is the transition moment given by

$$Q_{0\to l} = \int \Psi_0 er \Psi_l dv \ . \tag{28}$$

---

[34] R. Pariser, J. Chem. Phys., 24, (1956), p. 250.

CHAPTER II

METHODS AND MATERIALS

A. Solvents

1. Hydrocarbons: Phillips pure grade 3-methylpentane (3-MP) and isopentane (IP) were washed by stirring them continuously for approximately 12 hours with fuming sulfuric acid. They were rinsed twice with water, twice with saturated sodium carbonate solution and then twice with water again. The solvents were dried over anhydrous magnesium sulfate for 24 hours and then were distilled at the rate of 10-20 drops per minute. The still consisted of an electrically heated two-liter single necked flask with a 30 inch distillation column filled with glass beads. Solvents were considered to be sufficiently pure when there was no appreciable absorption at energies less than 47,600 $cm.^{-1}$ and there was no appreciable emission. In the isolated cases in which benzene was used as a solvent, Fisher certified reagent grade benzene was used without further purification.

2. Ethyl Alcohol: 95% alcohol from U.S. Industrial Chemical Co. was used without purification.

3. Methyl Alcohol: Fisher Certified Reagent grade was used without further purification.

4. Mixed Alcholic Solvent: Hartmann-Leddon Co. prepared fluorometric grade mixture of methyl, isopropyl and ethyl alcohols.

B. Compounds

1. 2-phenylnaphthalene: K&K Laboratories, Inc. commercial grade purified by many techniques still contained anthracene as an impurity. Pure synthetic 2-phenylnaphthalene was prepared by the following method. The di-2-naphthoyl peroxide for the synthesis was prepared by the procedure described by Kharasch and Dannley.[35] Approximately 35 g. of 2-naphthoyl chloride dissolved in 50 ml of anhydrous acetone was slowly added to an agitated suspension of 7.4 g. of sodium perioxide in 100 ml of anhydrous acetone at 0°C. After the addition was complete, one millileter of water was added and stirring was continued at 0°C overnight. The di-2-naphthoyl peroxide separated when the solution was poured into 200 ml of ice water. The peroxide was filtered, washed with dioxane and petroleum ether and dried under vacuum. The peroxide was reacted with benzene as described by Hey and Walker.[36] Approximately 20 g. of the di-2-naphthoyl peroxide was dissolved in 500 ml of benzene and the resulting solution was refluxed for 36 hours. The excess benzene was distilled off and the product was boiled with 10%-aqueous-alcoholic sodium hydroxide for 3 hours. The alcohol was distilled off and the water was decanted.

---

[35] Kharasch and Dannley, J. Org. Chem., 10, (1945), p. 410.

[36] D. H. Hey and W. E. Walker, J. Chem. Soc., (1948). p. 2217.

The solid product was dried under vacuum. Sublimation at atomospheric pressure produced large plates of 2-phenylnaphthalene melting at 104°C. The literature m.p. is 103-4°C.

2. 2'-methyl-2-phenylnaphthalene: This compound was synthesized by James Harris[37] and was used without further purification.

3. 1-fluoro-2-phenylnaphthalene: This compound was prepared from 2-phenylnaphthalene by a four step reaction sequence. The procedure outlined by Hey and Lawton[38] was used for preparation of 1-amino-2-phenylnaphthalene. The method consisted of nitration of 2-phenylnaphthalene with HNO_3 in glacial acetic acid and subsequent reduction to the amine. Approximately 8 g. of the 1-amino-2-phenylnaphthalene was diazotized by 3 g. of $NaNO_2$ in 50 ml of 49% HF solution at 0-5°C. To the diazotized mixture was added 20 g. of $NaBF_4$ in 50 ml of water at 0-5°C. The yellow precipitate of the diazonium fluoroborate that formed was separated by filtration, washed with methyl alcohol and ether, and dried under vacuum. The product was decomposed by heating and the 1-fluoro-2-phenylnaphthalene was steam distilled from the decomposition products. Four crystallizations from ethyl alcohol gave white needles melting at 60°C. Carbon-hydrogen analysis confirmed the empirical formula of the compound.

4. 1-chloro-2-phenylnaphthalene and 6-bromo-2-phenylnaphthalene: These compounds were synthetic samples prepared by D. H. Hey and co-

---

[37] James L Harris, loc. cit.

[38] D. H. Hey and S. E. Lawton, J. Chem. Soc., (1940), p. 378.

workers who kindly donated them for this research. The reported melting points were 82°C for the 1-chloro derivative and 132°C for the 6-bromo derivative.

5. 1-bromo-2-phenylnaphthalene: This compound was prepared by the method outlined by Hey and Lawton.[39] To a solution of 6 g. of bromine in 36 millileters of glacial acetic acid was added 6 g. of powdered 2-phenylnaphthalene. The solution was agitated at room temperature for 10 hours and at 50°C for 1 hour. The resulting mixture was poured into ice water where a viscous semi-solid formed. This material was dried, vacuum sublimed and finally crystallized several times from methanol. The final product melted at 66°C as reported by Hey and Lawton.

6. 2'-fluro-2-phenylnaphthalene: Approximately 20 g. of di-2-naphthoyl peroxide was prepared in the same manner as that described for the 2-phenylnaphthalene synthesis. The peroxide was added slowly over a period of 2 hours to 300 mls of refluxing fluorobenzene. The mixture was allowed to reflux for 3 days continuously, after which the fluorobenzene was removed by distillation. The remaining solid residue was washed several times with hot sodium carbonate solution and was dried under vacuum. The product was separated from 2-naphthoic acid impurity by sublimation and elution from an alumina column with CCl_4. Several slow crystallizations from ethyl alcohol gave a product

---

[39] D. H. Hey and S. E. Lawton, loc. cit.

with a melting point of 74-75°C. Carbon-hydrogen analysis confirmed the empirical formula of the product.

7. 2'-chloro- and 4'-chloro-2-phenylnaphthalene: These compounds were prepared by the same reaction sequence used for the preparation of the 2'-fluoro-derivative except that the peroxide was reacted with chlorobenzene instead of fluorobenzene. After the reaction product was washed with hot sodium carbonate and dried, a semi-solid product was separated by vacuum distillation into two fractions. The higher boiling fraction yielded 4'-chloro-2-phenylnaphthalene melting at 137-138°C after four crystallizations from ethyl alcohol. The literature melting point for this compound was 136°C. The lower boiling fraction was eluted from an elumina column with petroleum ether. The resulting product after several crystallizations from alcohol was 2'-chloro-2-phenylnaphthalene melting at 71-2°C. Carbon-hydrogen analysis confirmed empirical formulas of the isomers.

8. 2'-bromo- and 4'-bromo-2-phenylnaphthalene: These compounds were prepared by the same reaction sequence that was used for the preparation of the 2'-chloro derivative except that the peroxide was reacted with bromobenzene instead of chlorobenzene. After the reaction product was washed with sodium carbonate solution and dried, it was separated from tarry impurities by vacuum distillation. The product crystallized after several days and was recrystallized from petroleum ether. Fractional crystallization of the residue from alcohol yielded plates of 4'-bromo-2-phenylnaphthalene melting at 135-136°C. The material remaining in petroleum ether solution was concentrated and

crystallized. After several crystallizations from alcohol the 2'-bromo-2-phenylnaphthalene was isolated with a melting point of 81-2°C. Carbon hydrogen analysis confirmed the empirical formulas of the isomers.

9. 1,2-benzfluorene: K&K Laboratories, Inc. commercial grade that had been previously vacuum sublimed twice was subjected to a single atmospheric pressure sublimation. This was sufficient to remove extraneous emissions from the compound.

10. Fluoranthene: This synthetic compound was supplied by Dr. Milton Orchin of the University of Cincinnati.

C. Spectroscopic Measurements

1. Ultraviolet Absorption Measurements: The absorption spectra of the compounds studied were measured by the means of Cary Model 14 Recording Spectrophotometer. The wavelength measurements were good to ± 3 A. when read from the wavelength indicator. The resolving power of the monochromator is reported by the manufacturer to be 1 A. throughout the range 1900-13,000 A.

The solvents used for this work were spectroscopically pure as described previously. The temperature was not controlled, however, room temperature was about 25°C as controlled by the room thermostat. Absorption spectra of all the compounds in rigid glassy solution at 77°K were obtained. These spectra were measured by the method described by Williamson.[40] The solvent used for the low temperature measurements

---

[40] L. H. Williamson, Ph.D. Dissertation, Louisiana State Universtiy, Baton Rouge, (1965), p. 22.

was a 1:6 mixture of 3-methylpentane: isopentane (3-MPIP). This mixture forms a very transparent rigid glass without shattering the delicate 1 cm. square quartz absorption cells used for the measurements. The technique used was to suspend the sample cell inside the liquid nitrogen dewar by use of a long glass rod terminated by a ground glass stopper of appropriate size to fit the sample cell. A small piece of tygon tubing served to prevent the sample cell from separating from the glass stopper. No dewar was placed in the reference compartment. Only a sample cell filled with solvent at room temperature was used as a reference.

2. Emission Measurements Using the Cary Model 14 Recording Spectrophotometer: The Cary Model 14 Recording Spectrophotometer was used as a detector for recording all emission spectra reported in this research. The emitted radiation from the sample enters the Cary spectrophotometer through the visible light source lens on the back of the instrument. The sample holder that is attached in place of the visible light source is diagrammed in Figure 2. The sample holder adaptor is designed in such a manner that the emitting sample is located at the focal point of the visible optical system. The samples were excited by use of the specially designed Cary 15 monochromator coupled to a 250 watt xenon arc light source. The exciting monochromator was carefully positioned to give front surface illumination of all samples when the sample tube was centered in the dewar.

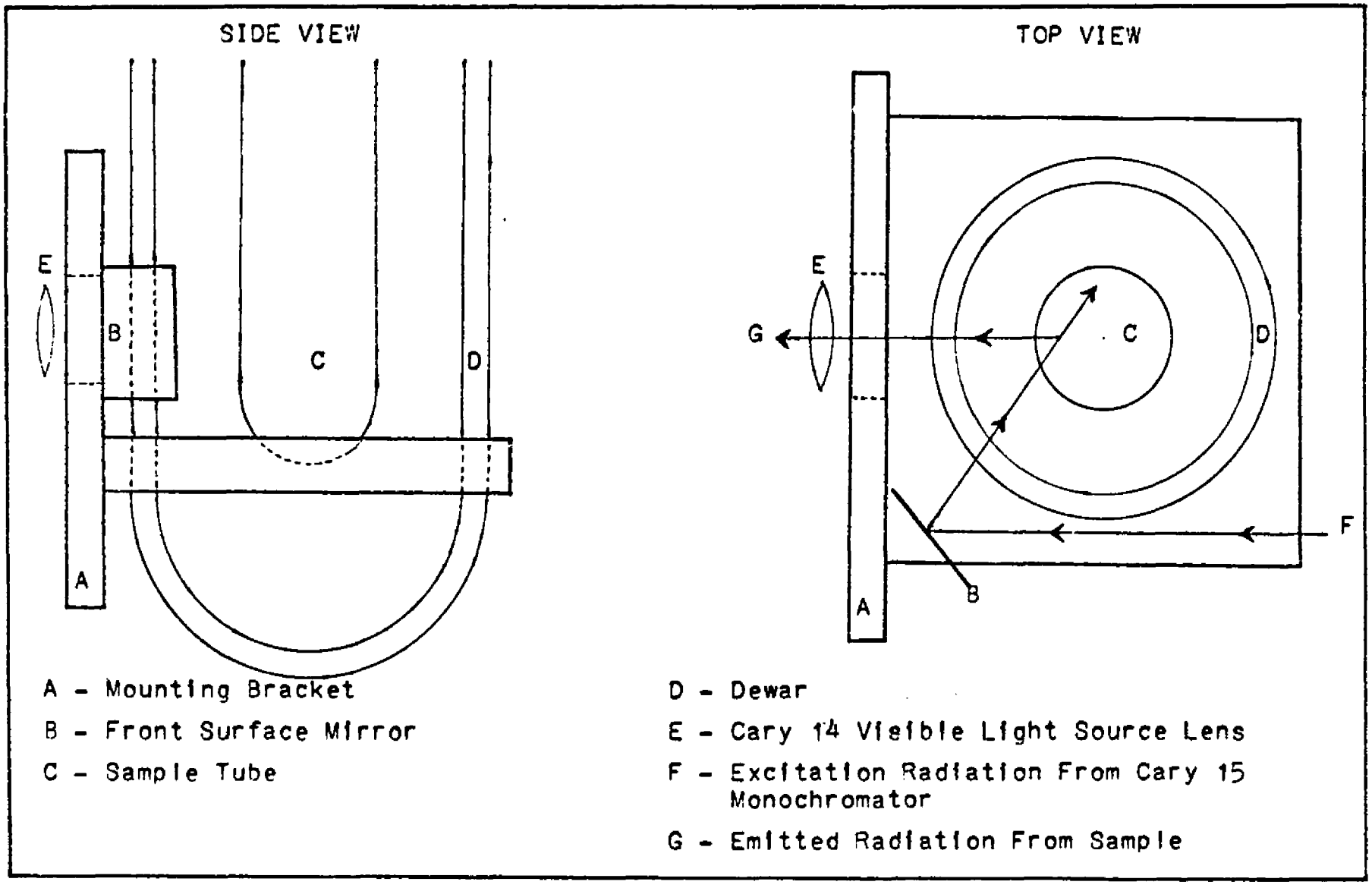


FIGURE 2. Cary 14 Total Emission Apparatus

For most samples the fluorescence spectra were recorded at 77° K. All samples had phosphorescences of sufficient intensity to be measured by excitation from the Cary 15 monochromator. When it was necessary to isolate the phosphorescence emission, a rotating disc Becquerel type phosphoroscope was used in conjunction with excitation by the full intensity of a General Electric AH-6 mercury arc. The emissions were all measured in rigid glassy 3-methylpentane except in a few isolated cases in which mixed alcoholic glass or solid benzene were used for specific purposes.

3. Fluorescence and Phosphorescence Quantum Yield Measurements: Quantum yield measurements were made on all the compounds studied in this research. These were all made with the aid of the total emission apparatus described in Figure 2. In addition a small plastic spider with arms extending from the testube to the walls of the dewar was attached to the sample tube to keep it perfectly centered in the dewar for each measurement. These measurements involved comparison of the areas under the emission curves under conditions of equal absorption of excitation energy. All the compounds studied could be efficiently excited in the $^1L_a \leftarrow {}^1A$ absorption band at 2800 A. Since there was some variation in the extinction coefficients of the compounds at 2800 A., the concentrations were adjusted to give equal absorptions at 2800 A. Each time a series of compounds was measured a standard (Naphthalene) was also included to correct for possible changes in intensity of the light source. The same sample tube was used for all measurements and it was oriented in the same direction each time.

All samples were allowed to cool 15 minutes at liquid N_2 temperature after the solution was degassed twice. After the emissions were recorded for the standard and unknowns under these carefully controlled conditions, the areas under the curves were determined by weighing. These areas were corrected to the same slit width as that used for naphthalene by assuming the intensity to be proportional to the square of the detector slit width. This assumption has been found to be good for slit widths of 2 mm or less. When it was necessary to use wider slits, the results are reported as only approximations. The quantum yields were determined by comparing the corrected areas with the corresponding area of the standard and assuming the quantum yield of emission to be proportional to the corrected areas.

Many different quantum yields are reported for naphthalene in the literature.[41,42,43] There is a lack of agreement between the values reported. Because of this the quantum yields of 1,2-benzfluorene calculated in the following manner were used as standards. Since 1,2-benzfluorene has a very high fluorescence yield and since nearly all quenching at 77°K occurs from the triplet state, it was assumed that $\Phi_P + \Phi_F = 1$ for 1,2-benzfluorene. The area under the phosphorescence emission curve of 1,2-benzfluorene was corrected to the same slit width as that of the fluorescence and a correction for phototube response from the RCA phototube manual was applied. Using

---

[41] Gilmore, Gibson and McClure, J. Chem. Phys., 20, (1952), p. 829.

[42] V. L. Ermolaev and K. K. Svitashev, Opt. Spectry., 7, (1959), p. 399.

[43] Parker and Hatchard, Analyst, 87, (1962), p. 664.

these corrections and the appropriate areas, it was found that Φ_P/Φ_F = .00448 for 1,2-benzfluorene. Solving the two equations for Φ_P and Φ_F gave values of 0.0045 and 0.995 respectively. Using these yields as standards gave values for naphthalene of Φ_P = 0.0105 and Φ_F = 0.449. The value of Φ_P/Φ_F for naphthalene calculated by this method agrees within 10% of the recent value reported by Parker and Hatchard.[44] All values for quantum yields reported in this work are based on the yields calculated for 1,2-benzfluorene. From the limited data available the reproducibility is estimated to be within 10% except for the values reported as approximations.

4. Phosphorescence Lifetime Measurements: The phosphorescence lifetimes were determined by the following procedure for all the compounds studied. The shortest lifetime measured was 48 milliseconds, therefore, all could be measured by use of a mechanical rotating disc Berquerel type phosphoroscope. All samples were dissolved in 3-methylpentane, degassed five times and allowed to freeze 15 minutes at 77°K to insure maximum rigidity of the glass. The phosphorescences were excited by the full intensity of an AH-6 mercury arc equipped with a guillotine type shutter. The emission was detected by a 1P28 photomultiplier tube connected to an Aminco amplifier unit. The decay time of the amplifier circuit in the range used was found to be very short compared to the phosphorescence lifetimes and should introduce no error in the measurements. The amplifier

---

[44] Parker and Hatchard, loc. cit.

output was displayed on a Techtronix Type 536 oscilloscope equipped with a C-12 polaroid-back camera. The scan rates on the scope were calibrated at low rates with a stopwatch and at fast rates by use of a 60 cps AC signal.

The decay of the phosphorescence emission for each sample was photographed from the oscilloscope tube after the shutter on the AH-6 excitation lamp was closed. The lifetimes were determined from the photographs by carefully measuring the time required for the phosphorescence intensity to decrease to 1/e of its original value.

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

A. Spurious Emissions from 2-Phenylnaphthalene, 1,2-Benzfluorene and Fluoranthene

Two fluorescence emissions and two phosphorescence emissions have been reported for 2-phenylnaphthalene and 1,2-benzfluorene by Harris[45] and for fluoranthene by Ory[46] and Wharton.[47] Since multiple fluorescence or phosphorescence emissions are not normally observed for aromatic hydrocarbons, the phenomena, if real, deserve considerable experimental and theoretical consideration. The original objective of this experimental work was to confirm and better characterize the dual emission phenomenon.

The electronic absorption spectrum of 2-phenylnaphthalene reported by Harris differs from the spectrum previously reported by Friedel.[48] Harris observed a new transition having vibrational bands at 3770, 3540 and 3400 A. The second fluorescence emission reported for 2-phenylnaphthalene shows a close mirror image relationship to this

---

[45] James Harris, loc. cit.

[46] Horace Ory, loc. cit.

[47] James H. Wharton, loc. cit.

[48] R. A. Friedel, et. al., J. Am. Chem. Soc., 70, (1948), p. 199.

absorption and was assigned by Harris as a radiative transition from the excited state at 3770 A. to the ground state of 2-phenylnaphthalene. Harris was unable to remove or alter the intensity of the new absorption or second emission by purification, and thus attributed the absorption and emission to 2-phenylnaphthalene.

As a preliminary experiment Harris' absorption measurements on 2-phenylnaphthalene were repeated. Purification of 2-phenylnaphthalene was attempted by the zone-melting technique. During the zone-melting process, a zone appeared in the lower half of the tube that had a more crystalline appearance than the sample on either end of the sample tube. Equally concentrated solutions in methyl alcohol were prepared with sample collected from the crystalline zone and sample collected from the top of the tube. The absorption spectra were measured for both samples under identical conditions. The two samples did not give the same absorption spectrum. The intensity of the new long wavelength transition differed significantly between the two samples; the intensity was greater in the sample collected from the top of the zone-melting tube. Substantially less variation was observed in the intensities of the remaining absorption bands; the remaining bands were less intense in the top sample. These absorption measurements indicated strongly that the long wavelength absorption is due to an impurity. Further attempts to completely remove the long wavelength absorption by zone-melting and fractional crystallization of the collected crystalline sample were not successful.

As a separate approach to the problem synthetic 2-phenylnaphthalene was prepared as outlined in the materials and methods chapter. The absorption spectrum of the synthetic sample showed no absorption in the long wavelength region even when concentrations far greater than those of Harris' experiments were used. The remainder of the absorption spectrum of the synthetic sample was not different from that of the impure samples. In addition the total emission spectrum for the synthetic 2-phenylnaphthalene showed only a single fluorescence and a single phosphorescence. These emissions are discussed fully in section B of this chapter.

These experimental results show conclusively that the long wavelength absorption and the low energy fluorescence observed by Harris are due to an impurity and are not characteristic of the 2-phenylnaphthalene molecule.

The direct and indirect effects of impurities probably constitute the greatest source of error in molecular spectroscopic measurements. Thus, impurities should be identified whenever possible, especially when the impurity is difficult to remove or detect and is apt to be present in the source material. The following attempts were made to identify the impurity in 2-phenylnaphthalene.

The low energy absorption bands of the impurity in 2-phenylnaphthalene are essentially identical to those of the $^1L_a \leftarrow {}^1A$ transition of anthracene. Anthracene also has an intense band at 2500 A., which unfortunately cannot be observed because it is isoenergetic with an intense band in 2-phenylnaphthalene. The fluorescence

excitation spectrum of the low energy fluorescence emission observed from the impure 2-phenylnaphthalene indicates that a portion of the 2500 A. absorption band is characteristic of the impurity. From the absorption and excitation data above one would hastily conclude that the impurity was definitely anthracene. However, the fluorescence emission from the impurity is shifted approximately 490 $cm.^{-1}$ to the red of that of pure anthracene. Further close observation reveals that the major vibrational bands observed for the impurity in 2-phenylnaphthalene are isoenergetic with the low intensity vibrational bands in the pure anthracene fluorescence spectrum. These observations suggest that an intermolecular interaction or complexation exists between anthracene and 2-phenylnaphthalene. To test this theory solutions of 10^{-4} molar anthracene containing 1 mole percent (based on solute only), 2 mole percent and greater amounts of 2-phenylnaphthalene were made up and the fluorescence emissions of each mixture were recorded and were compared with that of pure 10^{-4} molar anthracene. Figure 3 shows the fluorescence emissions for pure anthracene and for the sample containing 2 mole percent 2-phenylnaphthalene. It is evident that the addition of 2-phenylnaphthalene causes an increase in the relative intensity of the weak vibrational bands of the anthracene emission. The phenomenon was observed in the cases of samples containing 1 mole percent and 2 mole percent 2-phenylnaphthalene, but was not observed for samples containing 5 mole percent or greater amounts of 2-phenylnaphthalene.

Although the data available are limited, they indicate that a complex is formed between 2-phenylnaphthalene and anthracene. The

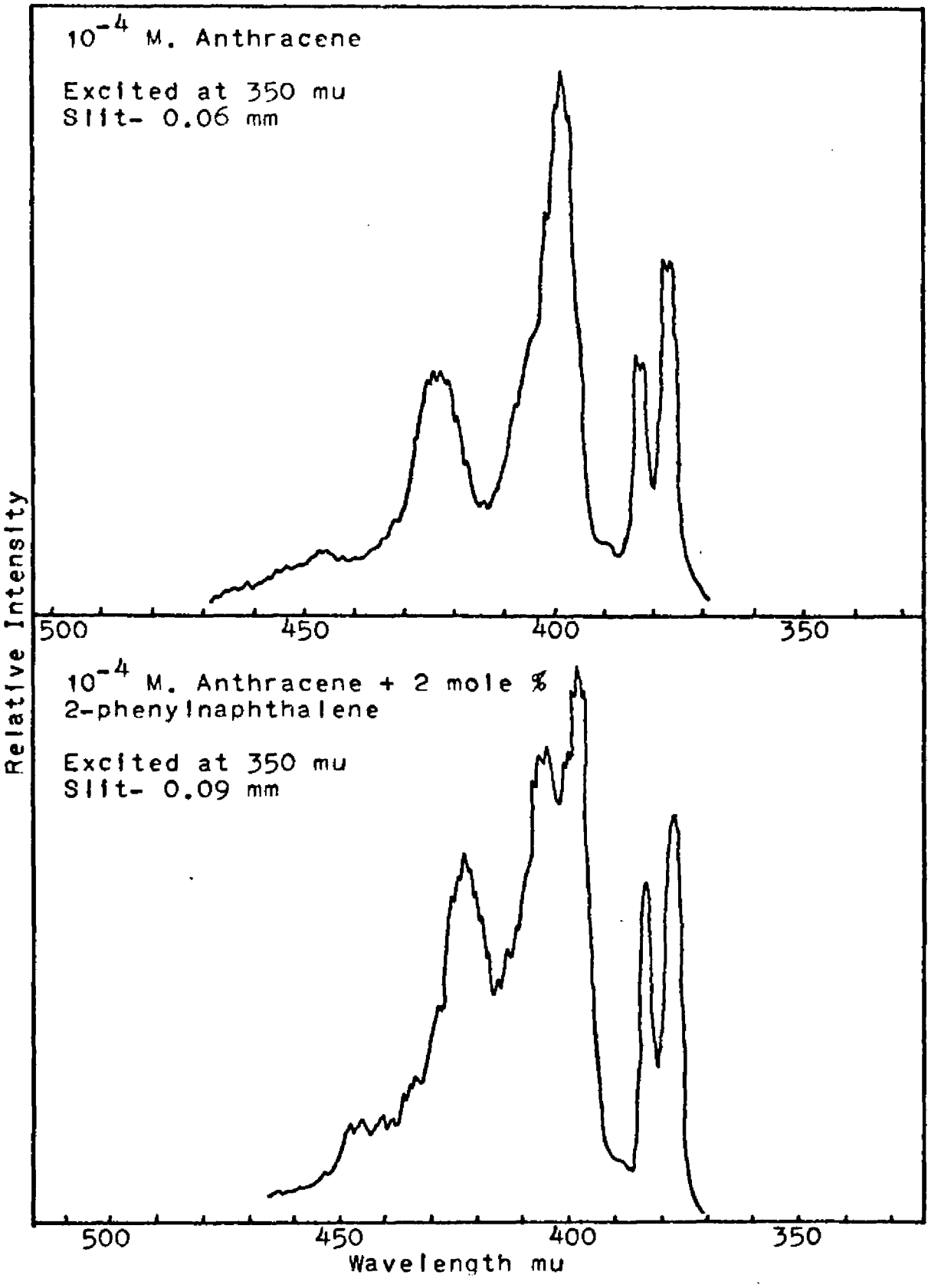


FIGURE 3. 77° K. Fluorescence of Pure Anthracene and Anthracene Containing 2 mole % 2-phenylnaphthalene in 3-methylpentane

origin of the forces responsible for the complexation is uncertain. In addition it is difficult to interpret the effect of 2-phenylnaphthalene upon the anthracene fluorescence emission. The effect does not appear to be a simple shift in energy of the total spectrum, but rather an intensification of the antisymmetric vibrational bands with a simultaneous decrease in the intensity of the symmetric vibrational bands. If the latter contention is correct, 2-phenylnaphthalene must have a pronounced effect on the geometry of the excited state of anthracene.

Regardless of the forces responsible for the complexation and the change in the fluorescence emission of anthracene, the fluorescence emission spectrum an anthracene in 2-phenylnaphthalene approaches that of the impurity present in commercial 2-phenylnaphthalene. Anthracene has also been observed as an impurity in fluorene[49] giving an apparent second fluorescence. It is interesting that the fluorescence emission observed in this case is almost identical to the impurity fluorescence from 2-phenylnaphthalene. Apparently fluorene perturbs anthracene in much the same way as does 2-phenylnaphthalene.

The experimental evidence indicates strongly that the impurity in 2-phenylnaphthalene is anthracene. Anthracene is a prime candidate for the impurity, since both compounds are obtained commercially from the distillation of coal tar. The melting and boiling points of 2-phenylnaphthalene are reported to be 104°C and 345°C respectively. Those of anthracene are 216°C and 340°C respectively.

---

[49] R. N. Nurmukhametov, G. V. Gobov, Opt. Spectry., 13, (1962), p. 384.

Harris also observed a previously unreported transition in 1,2-benzfluorene with an absorption maximum at 3750 A. He also observed a second fluorescence emission that apparently was a mirror image of this transition. Both the additional absorption and emission were removed by a single sublimation at atmospheric pressure. No attempt was made to identify the impurity in this case. The spectra of 1,2-benzfluorene will be discussed in more detail later.

In view of the impurities found in and removed from the previous compounds it was suspected that impurities were also responsible for the additional emissions of fluoranthene that were observed by Ory and Wharton. After attempts to purify the fluoranthene by sublimation an absorption spectrum exactly identical to that reported by Wharton was obtained. In spite of this result impurities were still suspected.

A sample of pure synthetic fluoranthene was obtained from Dr. Milton Orchin of the University of Cincinnati. Again the absorption spectrum was identical with that reported by Wharton, including the long wavelength absorption bands that had not been reported previously. The emissions of the synthetic fluoranthene were different in that only the low energy fluorescence and phosphorescence could be observed. For comparative purposes the emissions from zone-refined fluoranthene previously prepared by Wharton were measured under conditions identical with those used for the measurements with the synthetic fluoranthene. The dual emissions were present in the zone-refined fluoranthene but not in the synthetic fluoranthene.

In view of this evidence one must conclude that the dual emissions observed for fluoranthene were due to an impurity. The impurity phos-

phorescence in fluoranthene is almost identical with that of phenanthrene but is slightly red shifted as was that of anthracene in 2-phenylnaphthalene. Phenanthrene is a likely candidate as an impurity in fluoranthene, since both are commercially obtained from the same coal tar fraction. The melting and boiling points of fluoranthene are reported to be 111°C and 375°C respectively. Those of phenanthrene are 101°C and 340°C respectively. No further attempts were made to identify this impurity.

B. Spectra of 2-Phenylnaphthalene

The absorption spectra of synthetic 2-phenylnaphthalene in 3-MP at room temperature and in 3-MPIP at 77°K are shown in Figure 4. The room temperature crystal absorption is also shown for the low energy region. The crystal absorption spectrum is not a single crystal absorption but that of poly-crystalline 2-phenylnaphthalene supported between two quartz plates.

At least four transitions are observed in the room temperature solution spectrum. The $^1L_b \leftarrow {}^1A$ transition appears in the region of 3200 A. as a shoulder on the $^1L_a \leftarrow {}^1A$ transition, which has its maximum at 2870 A. The $^1B_b \leftarrow {}^1A$ band appears at 2500 A. and a band tentatively assigned as the $^1C_b \leftarrow {}^1A$. band has its maximum at 2120 A. It is important to note for future reference that the $^1C_b \leftarrow {}^1A$ band consists of a single peak at room temperature. The extinction coefficient of this band is observed to be somewhat less than that of the $^1B_b \leftarrow {}^1A$ band for 2-phenylnaphthalene.

The absorption frequencies and extinction coefficients measured for 2-phenylnaphthalene are given in Table I.

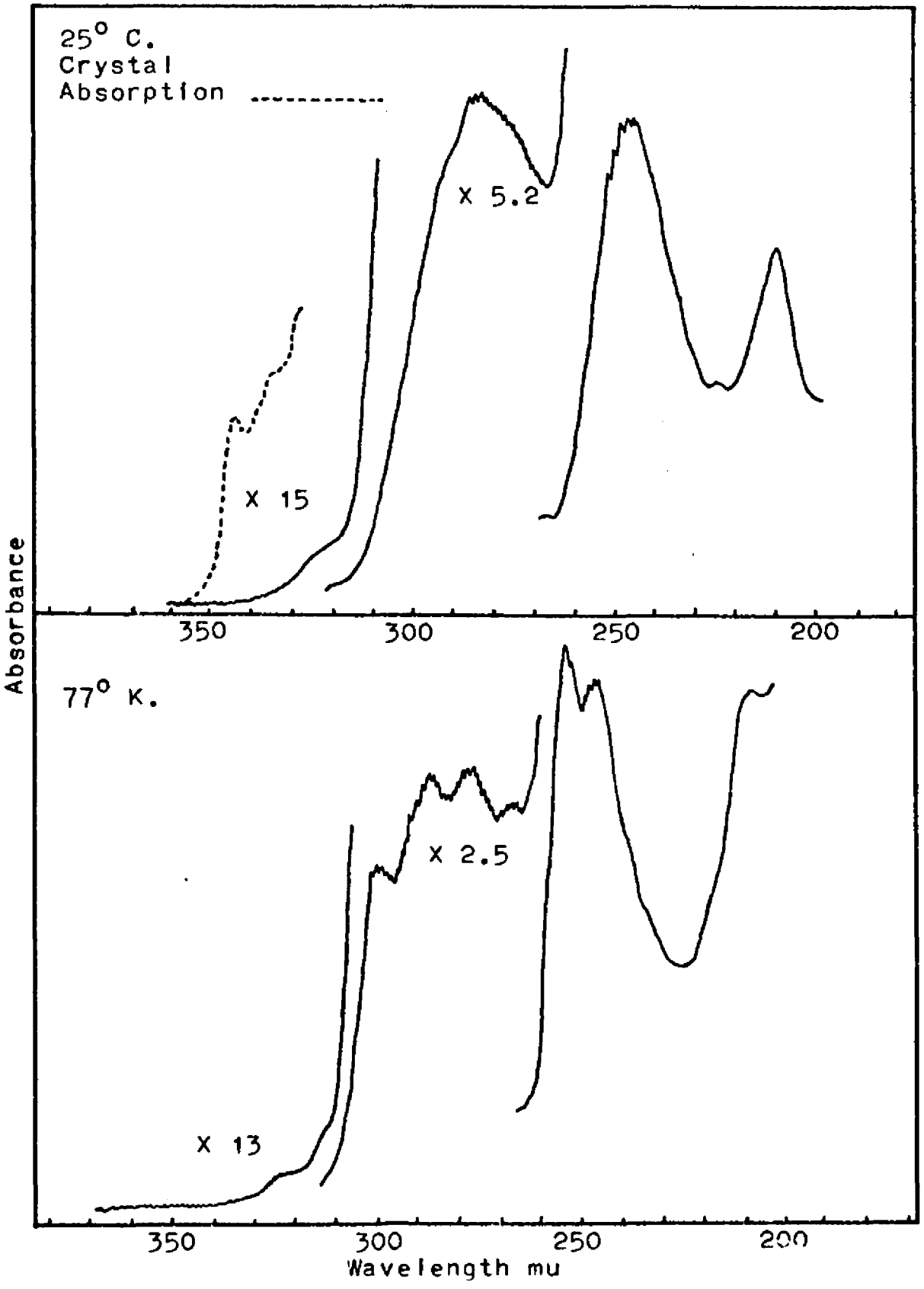


FIGURE 4. Room Temperature and 77° K. Absorption of 2-phenylnaphthalene in Hydrocarbon

TABLE I

Absorption Frequencies and Extinction Coefficients of 2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)	$\Delta\nu$
3430	29,154	crystal	0
3325	30,075	crystal	921
2870	34,843	1.25×10^{4}	-
2500	40,000	5.67×10^{4}	-
2120	47,170	4.12×10^{4}	-

77°C in 3-MPIP

A	Cm.$^{-1}$	$\Delta\nu$
3225	31,008	0
3010	33,222	0
2890	34,602	1380
2780	35,971	2749
2680	37,313	4091
2550	39,215	0
2465	40,568	1353

There seems to be good agreement between the room temperature and 77°K absorption spectra of 2-phenylnaphthalene aside from the normal increase in vibrational structure at 77°K. The vibrational splittings in the 77°K spectrum are on the average about 1350 $cm.^{-1}$, while that in the room temperature crystal absorption spectrum was 921 $cm.^{-1}$.

X-ray diffraction studies[50,51] indicate that the crystalline state of biphenyl, a molecule analogous to 2-phenylnaphthalene, is planar or nearly so. Electron diffraction studies[52] show that in the vapor phase the planes of the phenyl ring lie at an angle of 42° to each other. This angle has been interpreted by Goodwin and Morton-Blake[53] to be the equilibrium position resulting from two factors, the tendency toward planarity due to the P_z-orbital overlap across the bond between the rings and the tendency toward non-planarity due to steric repulsion between the 2:2' and 6:6' hydrogen atoms. These authors have calculated the energy contribution from both factors and have arrived at an expression for the total energy of the system as a function of the angle θ between the phenyl ring planes. This energy function takes the form shown in Figure 5.

The authors estimate that the minimum in the zero point energy for planar biphenyl is 1 Kcal./mole higher than that for the molecule

---

[50] A. Hargreaves, S. Hasenrizvi, Acta. Cryst. 15, (1962, p. 365.

[51] G. B. Robertson, Nature, 191, (1961, p. 593.

[52] A. Almenningen, O. Bastiansen, Klg. Norske Videns Selsk. Skrifter, 4, (1958).

[53] T. H. Godwin, P. A. Morton-Blake, Theoret. Chim. Acta. 1, (1963), p. 458.

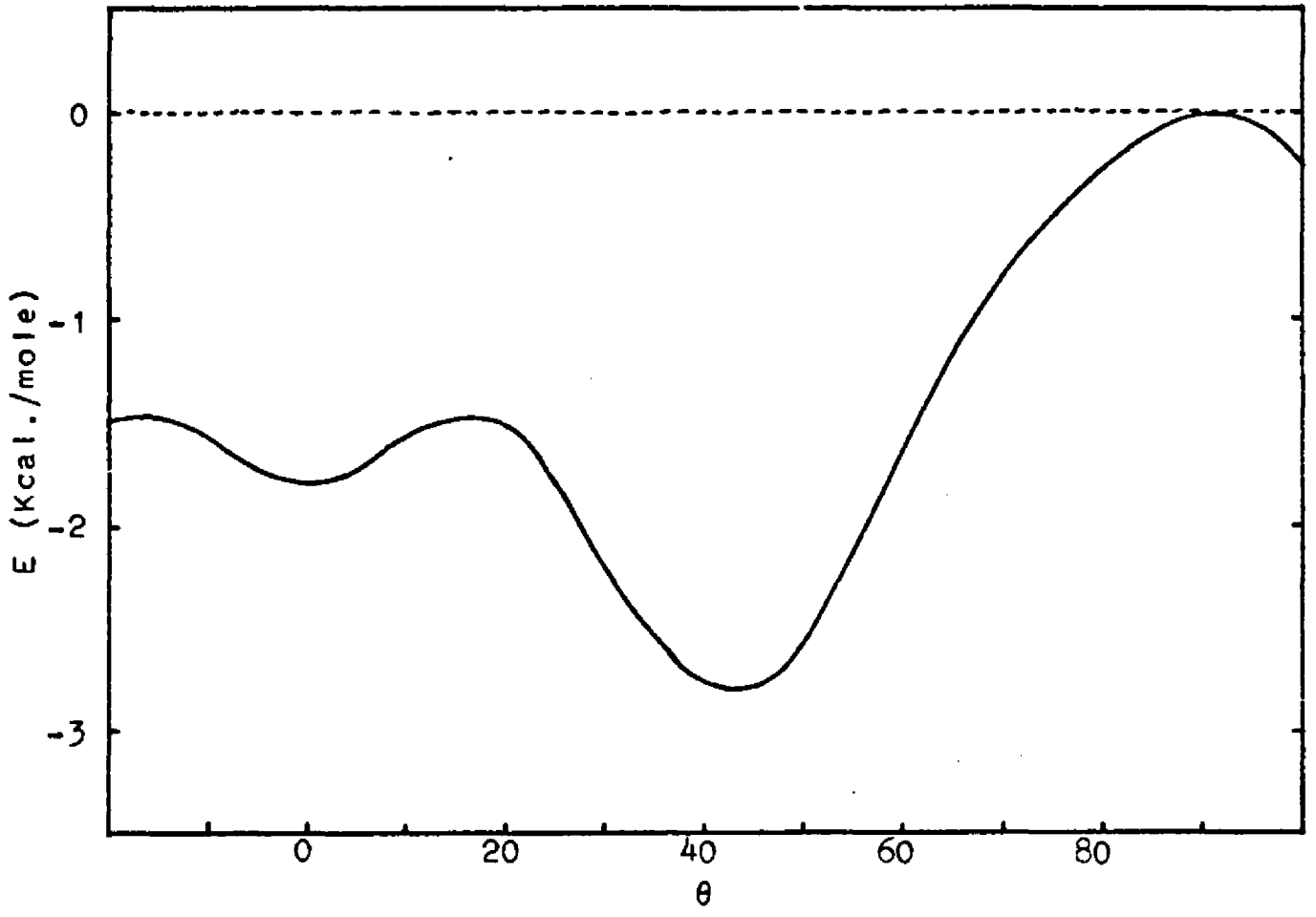


FIGURE 5. Total Energy of Biphenyl Versus θ

having a 42 degree angle between ring planes. The planar configuration observed in the crystal is attributed to a greater crystal binding energy for the planar molecule.

Geometrical and electrical considerations indicate that results similar to those for biphenyl should be observed for 2-phenylnaphthalene. The hydrogen repulsion terms should not be significantly different in the case of 2-phenylnaphthalene and the resonance stabilization term should be at least as great as that of biphenyl. Consideration of electron transfer between rings in terms of polar resonance structures indicates that the resonance stablization term between rings is greater for 2-phenylnaphthalene; more resonance structures are possible and the electron afinities are different in the case of 2-phenylnaphthalene. Thus, like that of biphenyl the zero point energy curve for 2-phenylnaphthalene should exhibit two minima, a shallow minimum at 0 degrees and a slightly deeper minimum between 30 and 40 degrees. The curve may be slightly unsymmetrical when plotted over 180° in the 2-phenylnaphthalene case. In the crystal the 2-phenylnaphthalene molecules should be planar while in the vapor or solution there should be a Boltzmann distribution of twisted molecules. Spectroscopic measurements should confirm these predictions.

In the 77°K absorption spectrum of 2-phenylnaphthalene in 3-MP (Figure 2) the first vibrational band of the $^1L_b \leftarrow {}^1A$ transition is observed at 3225 A. (31,010 $cm.^{-1}$). Increasing the concentration intensifies this weak band but the spectrum does not show any longer wavelength bands. However, if the solubility of 2-phenylnaphthalene

is exceeded, additional bands beginning at 3430 A. (29,150 cm.$^{-1}$) are observed. These longer wavelength bands coincide with those observed in the spectrum of the crystal. The band observed at 31,010 cm.$^{-1}$ in the solution spectrum is assigned to be the 0-0 band of the $^1L_b \leftarrow {}^1A$ transition for the molecule in solution and that at 29,150 cm.$^{-1}$ in the crystal spectrum is believed to be the corresponding band for the molecule in the crystalline matrix. The 1860 cm.$^{-1}$ red shift of the crystal spectrum from the solution spectrum is unusually large, and thus must be attributed to a change from a non-planar molecule in solution to a planar molecule in the crystal. In glassy solution at 77°K the electronic transition is from a non-planar equilibrium ground state to an identical (Franck-Condon) non-planar excited state while in the crystal the transition is from a planar ground state to the planar Franck-Condon excited state.

The vibrational frequency in the ^1L_b excited state is measured to be 920 cm.$^{-1}$ for the molecule in the crystal.

The fluorescence and phosphorescence emission spectra of 2-phenylnaphthalene in rigid glassy 3-MP at 77°K are shown in Figure 6. For comparison purposes the corresponding emission spectra of naphthalene are also shown. The spectroscopic data for 2-phenylnaphthalene are given in Table II and those for naphthalene are given in Table III. The fluorescence emission of 2-phenylnaphthalene in rigid glass apparently does not exhibit the typical mirror image relationship to the corresponding absorption in rigid glass. It is impossible to accurately determine the vibrational frequency of the ^1L_b excited

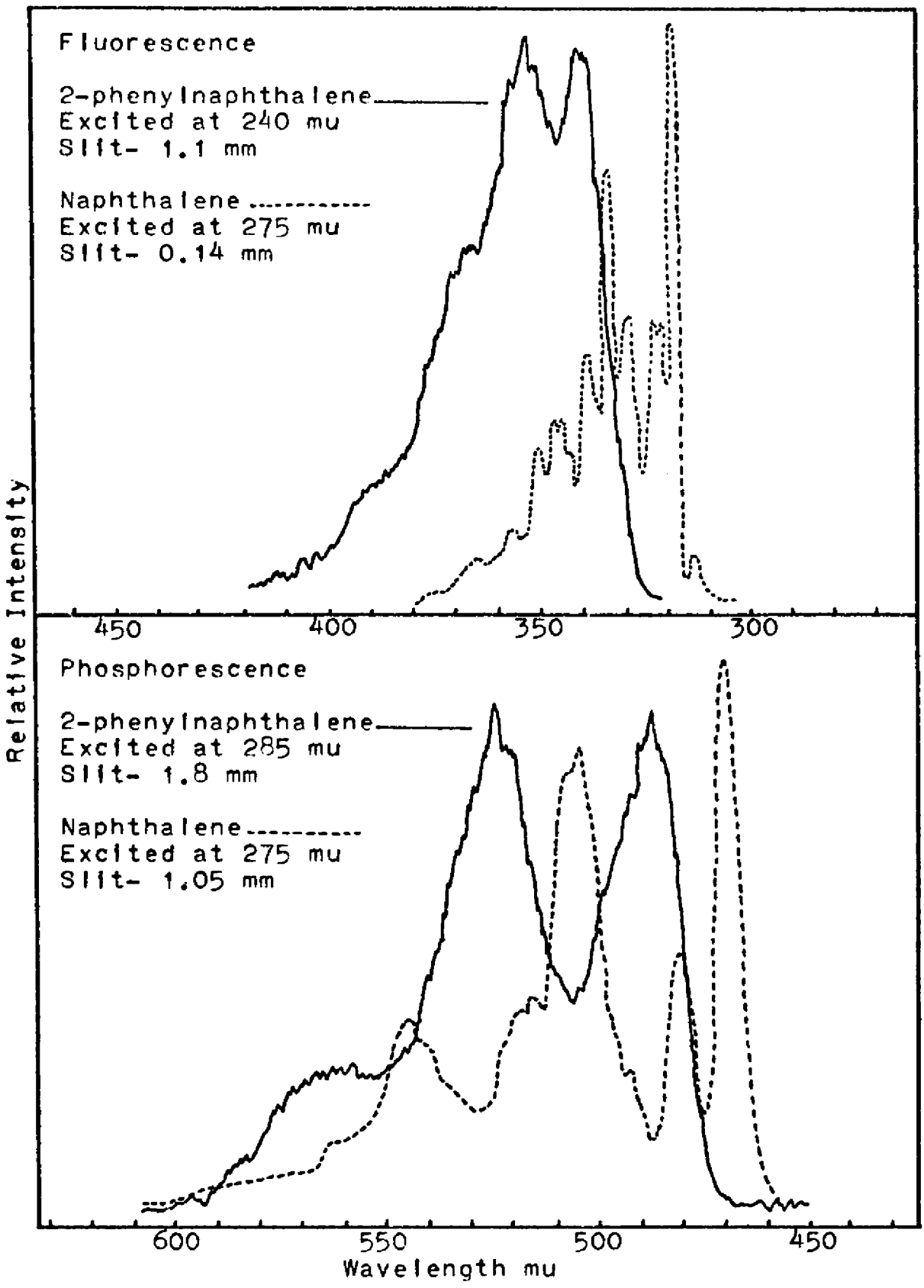


FIGURE 6. 77° K. Emission Spectra of Naphthalene and 2-phenylnaphthalene in 3-methylpentane

TABLE II

Emission Frequencies of 2-Phenylnaphthalene

Fluorescence

A	$Cm.^{-1}$	$\Delta \nu$
3420	29,240	0
3545	28,209	1031
3680	27,174	2066
3825	26,144	3096

Phosphorescence

A	$Cm.^{-1}$	$\Delta \nu$
4870	20,534	0
5230	19,120	1414
5650	17,699	2835

TABLE III

Emission Frequencies of Naphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3150	31,746	0
3200	31,250	496
3227	30,989	757
3243	30,836	910
3282	30,469	1277
3307	30,239	1507
3345	29,895	1851
3372	29,656	2090
3395	29,455	2291
3435	29,112	2634
3470	28,818	2928
3510	28,490	3256
3563	28,066	3680
3610	27,701	4045
3660	27,322	4424

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
4695	21,299	0
4820	20,747	552
5030	19,881	1418
5150	19,417	1882
5410	18,484	2815
5445	18,365	2934

state from the 77°K absorption spectrum. Estimation of these frequencies, however, gives an indication that the vibrational frequencies of the excited state may be higher than those of the corresponding ground state. The vibrational frequency in the ground state is measured to be 1030 $cm.^{-1}$. The 0,0 band in the fluorescence emission, observed at 3420 A. (29,240 $cm.^{-1}$) is displaced 1770 $cm.^{-1}$ from the 0,0 band in absorption.

Comparison of the fluorescence emission from the rigid glassy solution with the crystal absorption shows that an excellent mirror image relationship exists between the solution fluorescence and the crystal absorption. The 0,0 band of the fluorescence emission from the rigid glassy solution is only 90 $cm.^{-1}$ to the blue of the 0,0 band of the crystal absorption. Solvent effects predict that the solution spectrum should be slightly blue of the crystal spectrum. The vibrational frequency measured in the fluorescence emission (1030 $cm.^{-1}$) compares favorably with the vibrational frequency measured in the crystal absorption (920 $cm.^{-1}$); the ground state frequency is greater as it should be. In view of the previous assignments the fluorescence emission observed in rigid glassy 3-MP must correspond to a transition from a planar excited state to a planar ground state. Since the absorption in rigid glassy 3-MP was assigned to a non-planar to non-planar transition, the indication is that during the relaxation from the Franck-Condon excited state to the excited state to the equilibrium excited state the rings must rotate to a planar configuration. Thus the planar molecule must correspond to the lowest energy species for the excited state. The deepest minimum in the zero-point energy curve

must, therefore, occur at $\theta = 0°$. Based on the experimental observations the predicted zero-point energy curves for both the ground and excited electronic states have been constructed and are shown in Figure 7. The ground state minimum is shown arbitrarily at 38°. For the present the 38° angle is only an estimated value reflecting the belief that the resonance contribution should be slightly larger for 2-phenylnaphthalene than for biphenyl. Hence the equilibrium configuration would involve a smaller angle than the 42° angle observed in biphenyl.

In Figure 7 K_2 represents the 0,0 band of the $^1L_b \leftarrow {}^1A$ transition observed at 29,240 $cm.^{-1}$ in the low temperature fluorescence emission and K_1 represents the 0,0 band of the $^1L_b \leftarrow {}^1A$ transition observed at 31,010 $cm.^{-1}$ in the low temperature absorption spectrum in dilute solution. From the available data it is not possible to predict the shape of the zero-point energy curve in the excited state, however, the difference in energy between the zero-point energy of the Franck-Condon excited state and the zero-point energy of the equilibrium excited state can be determined. The difference in zero-point energies is given by the energy shift observed between absorption and emission (1770 $cm.^{-1}$ or 5.1 Kcal./mole) minus the difference in zero-point energies in the ground state. The difference in zero-point energies in the ground state has previously been estimated to be approximately 1 Kcal./mole. This gives 4.1 Kcal./mole for the difference in zero-point energy between the Franck-Condon excited state and the equilibrium excited state. This relatively large energy difference provides sufficient driving force for the non-planar to planar reorientation,

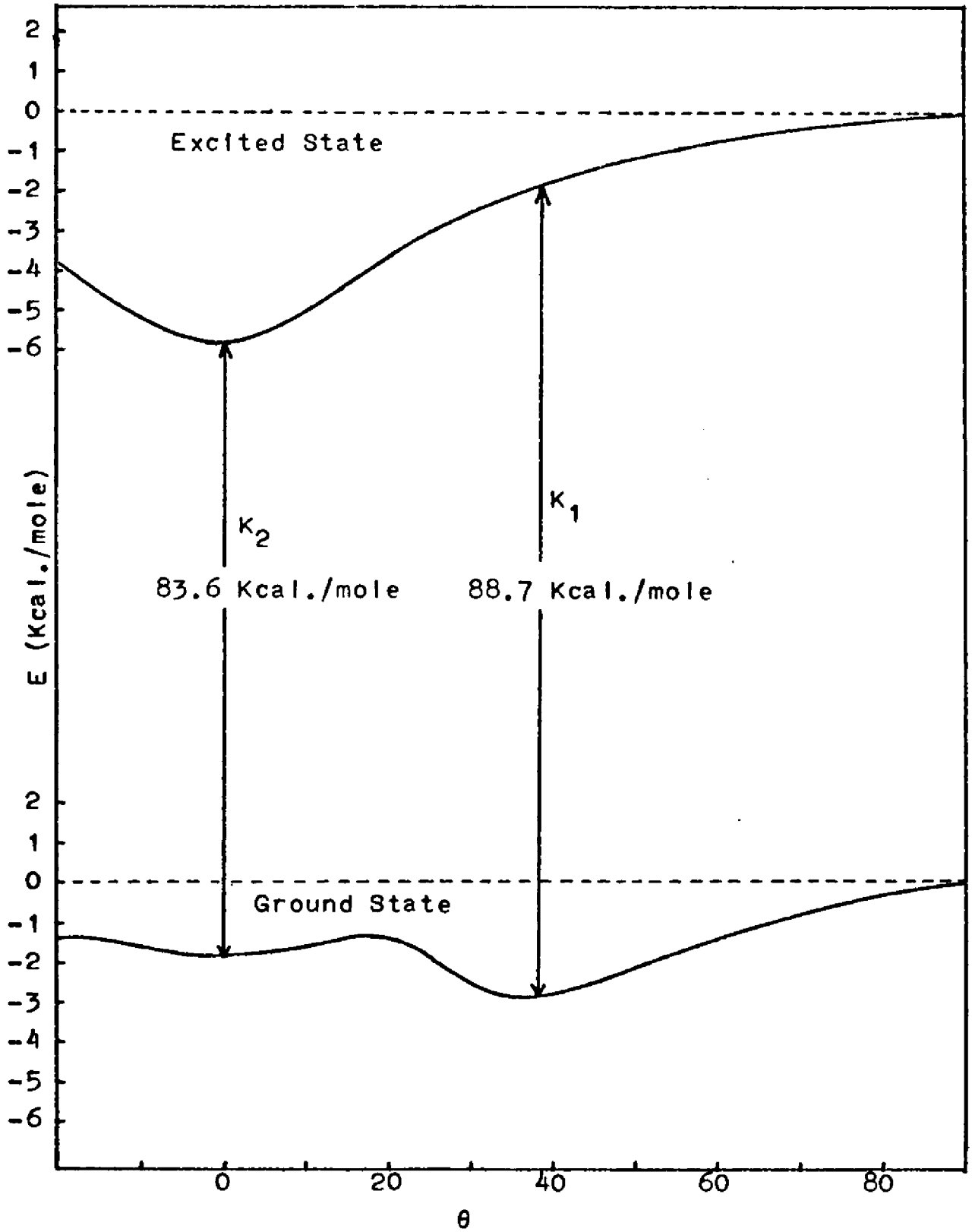
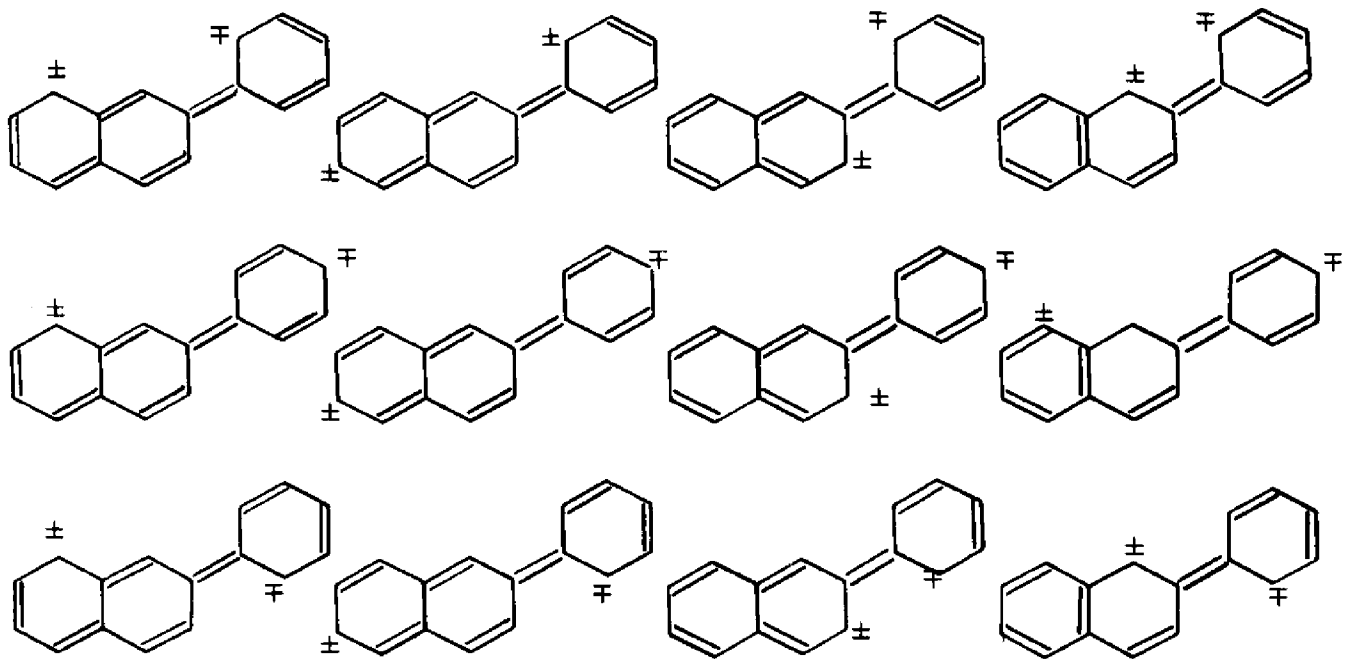


FIGURE 7. Zero-point Energy of 2-phenylnaphthalene Versus θ For Both Ground State and Excited State

however, it is difficult to understand how this reorientation is completed within the excited state lifetime ($\sim 10^{-6}$ sec.) and in rigid glassy medium at 77° K. Since essentially no emission is observed toward higher frequencies than the 0,0 band in the fluorescence emission, the reorientation must occur in less than 1/100 of the excited state lifetime ($\sim 10^{-8}$ sec.). This estimated maximum relaxation time is large compared with rotational and vibrational periods and thus many thousands of vibrations and internal rotations can occur during the time interval.

The large stabilization energy of the planar configuration relative to the non-planar configuration in the excited state indicates that there must be a significant increase in the double bond character of the bond between the two aromatic rings in the excited state. The following polar resonance structures in which a partial electronic charge is transferred from one aromatic ring to the other are consistent with the proposed increase in bond order.



There are two obvious experiments by which to prove that the equilibrium excited state of 2-phenylnaphthalene in glassy 3-MP is planar. If a potential barrier exists between the planar and non-planar configuration in the ground state, then it should be possible to convert the molecules to the planar configuration by optical pumping via the first excited singlet state. The change from non-planar to planar molecules could be verified by measuring the absorption spectrum before and after irradiation of the glassy matrix. This experiment was attempted on 2-phenylnaphthalene in glassy 3-MP at 77°K and no change in absorption was observed. However, the results do not imply that the interpretation of a planar excited state is incorrect, but rather that the rate of the planar to non-planar isomerism in the ground state is sufficiently rapid that a high population of the planar configuration could not be obtained under the experimental conditions. In a more rigid matrix and at lower temperature the experiment has a better chance for success.

The second experimental approach is simply to find a solvent matrix that is sufficiently rigid at 77°K to sterically prohibit the rotation from the non-planar to planar configuration in the excited state. Under these conditions the fluorescence emission should blue-shift and mirror image the absorption measured in the particular matrix. This experiment was attempted in mixed alcoholic glass and in solid benzene. In alcoholic solvent the normal red-shift (240 $cm.^{-1}$) relative to the fluorescence emission in 3-MP was observed and there

was a change in the Franck-Condon vibrational contour. No emission was observed to the blue and the measured vibrational frequency was that of the planar configuration. Essentially the same results were obtained for the solid benzene matrix with the exception that a few weak bands appeared to the blue of the main fluorescence and in the correct region to be emissions from a non-planar excited state. It was not possible to conclude that these bands were definitely due to emissions from a small fraction of non-planar molecules. They were definitely not benzene emission bands, however.

C. Spectra of 2'-Methyl-2-Phenylnaphthalene

A good method to test the hypothesis that 2-phenylnaphthalene is non-planar in the ground state but planar in the quiilibrium excited state is to compare its spectral properties with those of one of its derivatives that cannot achieve complete planarity. The simplest molecule for such a comparison is 2'-methyl-2-phenylnaphthalene. It is impossible for this molecule to become planar due to steric repulsion between the 2'-methyl group and either the 1 or 3-hydrogen atoms. The presence of the methyl group should seriously hinder any rotation of the phenyl ring.

The absorption spectra of 2'-methyl-2-phenylnaphthalene in 3-MP and 3-MPIP were measured at room temperature and 77°K respectively. These spectra are shown in Figure 8. The spectral data is given in Table IV. As in the case of 2-phenylnaphthalene, one observes the usual naphthalene-like transitions. the $^1L_b \leftarrow {}^1A$ transition appears

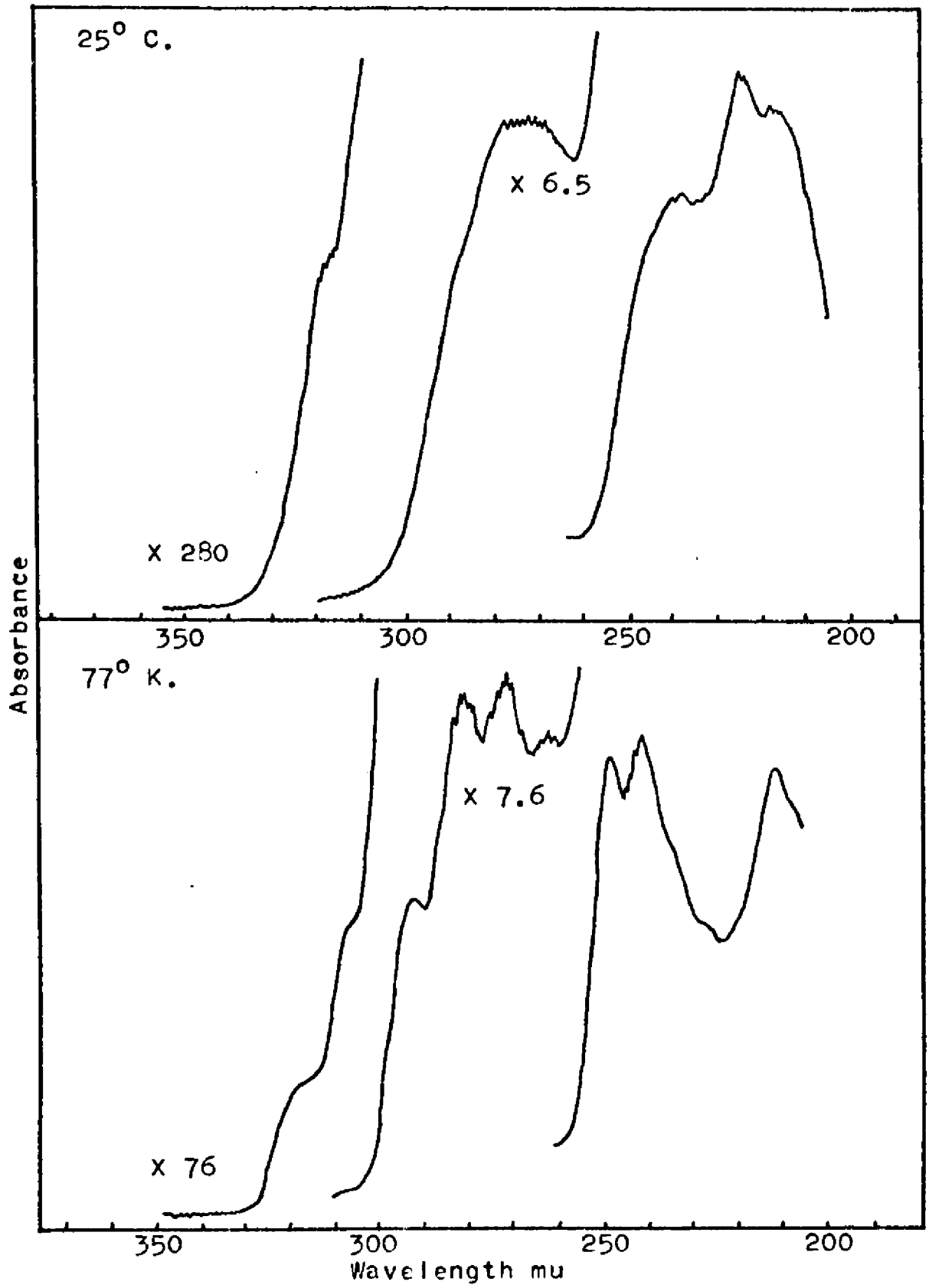


FIGURE 8. Room Temperature and 77° K. Absorption of 2'-methyl-2-phenylnaphthalene in Hydrocarbon

TABLE IV

Absorption Frequencies and Extinction Coefficients
of 2'-Methyl-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
2750	36,364	5.45×10^3
2400	41,667	2.75×10^4
2250	44,444	3.53×10^4
2180	45,872	3.53×10^4

77°K in 3-MP IP

A	Cm.$^{-1}$	$\Delta \nu$
3200	31,250	0
3180	31,447	197
3060	32,680	1430
2930	34,130	0
2825	35,398	1260
2730	36,630	2500
2640	37,879	3749
2500	40,000	0
2430	41,152	1152
2130	46,948	0

as a shoulder on the $^1L_a \leftarrow {}^1A$ transition, which has its maximum at 2750 A. at room temperature. The $^1B_b \leftarrow {}^1A$ and $^1C_b \leftarrow {}^1A$ transitions have their maxima at 2400 A. and 2180 A. respectively. In the room temperature spectrum but not in the low temperature absorption spectrum, a new transition is observed at 2250 A., which when combined with the $^1C_b \leftarrow {}^1A$ band gives an extinction coefficient greater than that for the $^1B_b \leftarrow {}^1A$ transition. There is also observed a decrease in the extinction coefficient of the $^1B_b \leftarrow {}^1A$ transition to 2.75×10^4 from a value of 5.67×10^4 from the same transition in 2-phenylnaphthalene. Some general conclusions concerning the probable origin of this band will be given after some of the properties of similar bands of the halogen derivatives have been discussed.

Comparison of the 77°K absorption spectrum of 2-methyl-2-phenylnaphthalene with that of 2-phenylnaphthalene shows that the 0,0 band of the $^1L_b \leftarrow {}^1A$ transition for 2'-methyl-2-phenylnaphthalene is blue shifted 240 $cm.^{-1}$ relative to that of 2-phenylnaphthalene. The indication is that 2'-methyl-2-phenylnaphthalene is slightly more out of plane than is 2-phenylnaphthalene in the electronic ground state. The crystal absorption spectrum of 2'-methyl-2-phenylnaphthalene does not reveal any longer wavelength bands of the type found in 2-phenylnaphthalene. This indicates, as expected, that 2'-methyl-2-phenylnaphthalene is non-planar in the crystalline state.

The 77°K fluorescence and phosphorescence spectra of 2'-methyl-2-phenylnaphthalene in rigid glassy 3-MP are shown in Figure 9 and the corresponding emission frequencies are given in Table V.

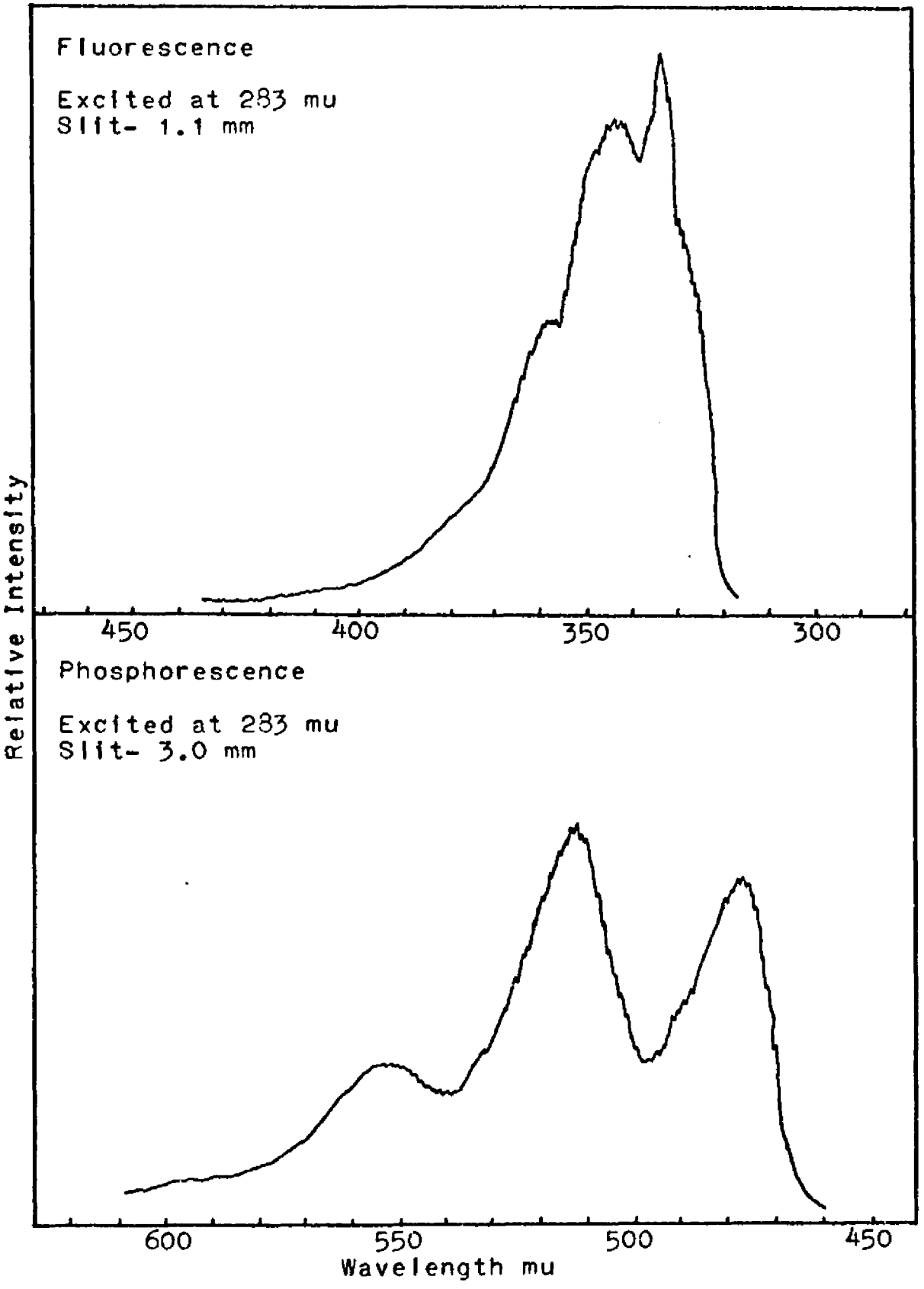


FIGURE 9. 77° K. Fluorescence and Phosphorescence of 2'-methyl-2-phenylnaphthalene in 3-methylpentane

TABLE V

Emission Frequencies of 2'-Methyl-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3280	30,488	0
3335	29,985	503
3455	28,944	1544
3585	27,894	2594
3725	26,846	3642

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
4785	20,899	0
5135	19,474	1425
5540	18,050	2849

The 0,0 band in the fluorescence emission of 2'-methyl-2-phenylnaphthalene, observed at 30,450 cm.$^{-1}$, is red-shifted 760 cm.$^{-1}$ from the 0,0 band measured in the absorption spectrum. This energy difference indicates that 2'-methyl-2-phenylnaphthalene, like 2-phenylnaphthalene, is closer to planarity in the equilibrium excited state than in the ground state, however, comparison of the shift observed for 2'-methyl-2-phenylnaphthalene (760 cm.$^{-1}$) with that observed in 2-phenylnaphthalene (1770 cm.$^{-1}$) indicates that 2'-methyl-2-phenylnaphthalene does not reach the planar configuration as does 2-phenylnaphthalene. The data is consistent with the added steric repulsion for 2'-methyl-2-phenylnaphthalene and the experimental evidence that 2-phenylnaphthalene is planar in the crystalline state while 2'-methyl-2-phenylnaphthalene is non-planar. In the absorption spectrum of 2'-methyl-2-phenylnaphthalene the vibrational frequency of the excited state is measured to be 1230 cm.$^{-1}$. That of the ground state is measured to be 1040 cm.$^{-1}$ in the fluorescence spectrum. As was estimated for 2-phenylnaphthalene the vibrational frequency of the excited state is higher than that of the ground state. Generally the vibrational frequency in the ground state is approximately 10 percent higher than that for the corresponding excited state. This again indicates that the equilibrium excited state is nearer the planar configuration than is the equilibrium ground state.

The experimental data determined in the case of 2'-methyl-2-phenylnaphthalene strongly support the interpretation of the 2-phenylnaphthalene spectra. Increasing the steric repulsion greatly reduces the contribution of the resonance stabilization term between rings.

The reduced contribution of the resonance stabilization to the pi electrons is reflected in the observed spectral shifts and vibrational frequencies.

D. Spectra of 1-Halo-2-Phenylnaphthalenes

In the study of 2'-methyl-2-phenylnaphthalene and 2-phenylnaphthalene, the determined absorption data from crystalline 2-phenylnaphthalene was limited to a portion of the $^1L_b \leftarrow {}^1A$ transition. Since the crystal is believed to keep the molecule planar in the ground state, the data for the planar configuration are severely limited. The transition energies and band contours for the higher energy transitions of the planar configuration are still unknown. These data are essential in the evaluation of resonance interactions and charge transfer contributions to higher energy states. In addition, the absorption and emission spectra of the planar 2-phenylnaphthalene derivative should contribute to the previous interpretation of the 2-phenylnaphthalene spectra. The theory is that the molecule with a planar equilibrium ground state in solution should have a red-shifted absorption spectrum, and more important, the absorption and fluorescence emission should exhibit a good mirror image relationship.

There are two methods by which to fix the 2-phenylnaphthalene molecule so that it can be maintained in a planar configuration. The first method is to chemically bond the ring planes together. An example of such bonding is 1,2-benzfluorene (see section E) in which a methylene group fixes the relative position of the rings in plane.

Weisburger, Weisburger and Ray[54] have recently shown by stereochemical measurements that fluorene has a planar configuration in solution. The second approach is to reduce the hydrogen-hydrogen repulsions which tend to keep the phenyl and naphthalene rings out of plane, or better yet to change the repulsion to an attraction. In the quantum mechanical description of the system such an attraction would be represented by a term that would support the resonance term in describing the tendency toward planarity. The writer contends that exchanging a halogen atom for the hydrogen atom in the 1-position of 2-phenylnaphthalene exchanges the hydrogen-hydrogen repulsion for a 1-halogen-2'-hydrogen attraction. The energies involved are small but sufficient to change the equilibrium ground state from the non-planar to the planar configuration at 77° K. These contentions are based on the geometry of 2-phenylnaphthalene, the electronegative character of the halogens (discussed below) and the spectroscopy of the 1-halo-2-phenylnaphthalenes.

A scale model of the planar 1-halo-2-phenylnaphthalenes is shown in Figure 10. The model is based upon the following data. All carbon-carbon bond lengths within the rings were assumed to be 1.40 A. and the bond between the rings was assumed to be 1.50 A. in length. This length was estimated from the interphenyl bond length in biphenyl, which was found to be 1.50 A. by x-ray crystal analysis.[55,56] All

---

[54] J. H. Weisburger, E. K. Weisburger and F. E. Ray, J. Am. Chem. Soc., 72, (1950), p. 4250.

[55] A. Hargreaves, S. Hasenrizvi, loc. cit.

[56] G. B. Robertson, loc. cit.

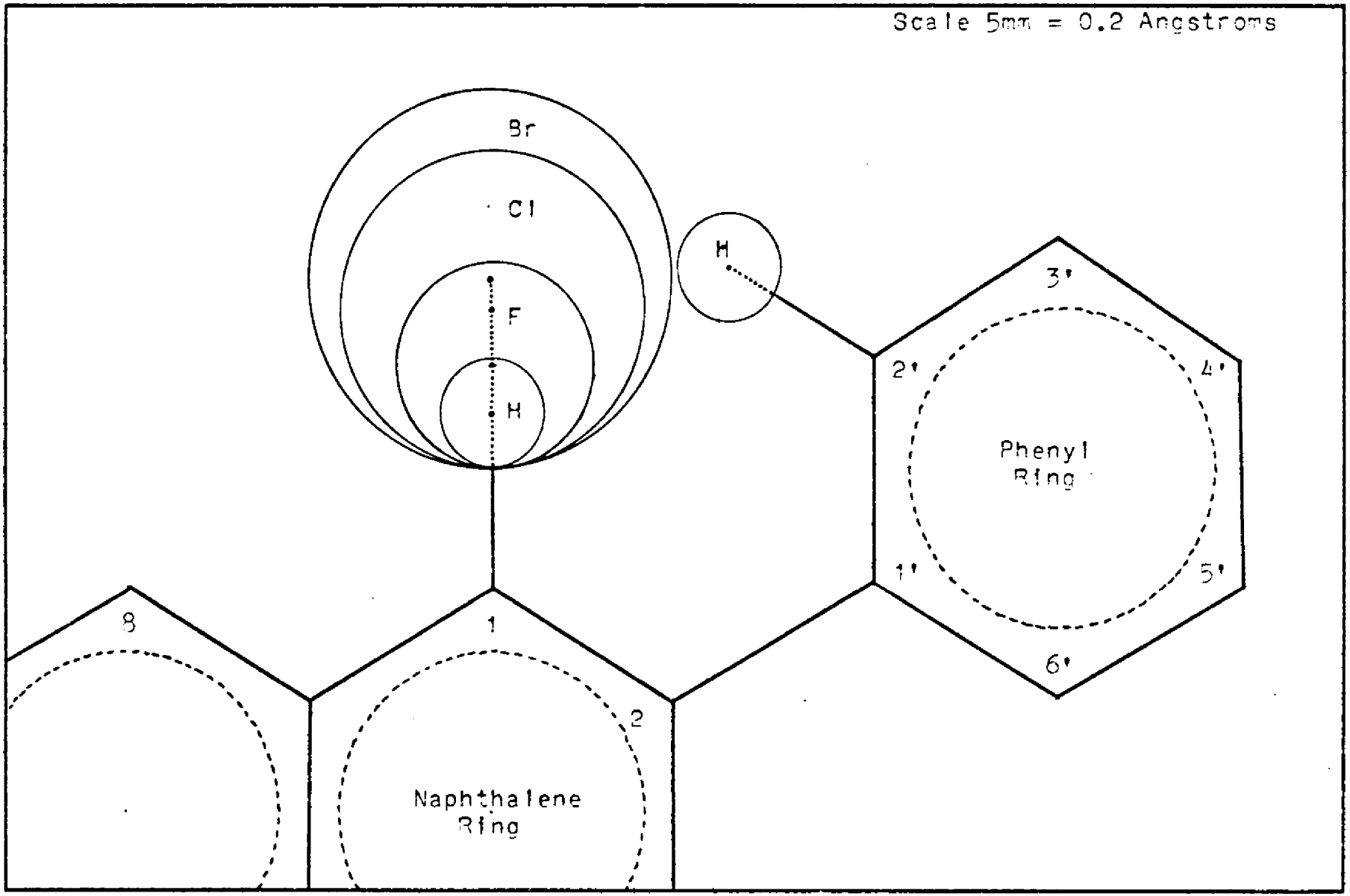


FIGURE 10. Geometry of Planar 1-Halo-2-phenylnaphthalene Derivatives

other bond lengths were based on the appropriate covalent radii. From the scale drawing the X----H internuclear distances in the planar configuration were measured to be 1.80 A., 1.66 A., 1.57 A. and 1.56 A. for X equals H, F, Cl and Br respectively. The C-X----H angles were measured to be 121°, 111°, 99° and 93° respectively for X equals H, F, Cl and Br. X-ray[57] and infrared[58] data have shown that molecules of the hydrogen halides exist as zig-zag chains of hydrogen bonded molecules at low temperature in the crystalline state. The distances between hydrogen bonded molecules are not much greater than the interatomic distances within the molecules. In addition, definite valence angles are observed in these hydrogen bonds. The exact values for the intermolecular distance in HCl and HBr are uncertain due to various phase transitions in these compounds. The H----F distance in solid HF[59] is approximately 1.34 A. The H-X----H angles were found to be 120.1°, 107° and 97° respectively for F, Cl and Br.

In the 1-halo-2-phenylnaphthalenes the magnitude of the hydrogen-halogen attraction should depend upon how closely the hydrogen-halogen angles and distances approach those measured for the hydrogen halides as well as upon the charge on the halogen and hydrogen atoms. Comparison of the data for the 1-halo-2-phenylnaphthalenes with that of the hydrogen

---

[57] M. Atoji and W. N. Kipscomb, Acta. Cryst. 7, 1954, p. 173.

[58] D. F. Hornig and W. E. Osberg, J. Chem. Phys. 23, 1955, p. 662.

[59] Y. K. Syrkin and M. E. Dyatkina, Structure of Molecules and the Chemical Bond, Interscience Publishers, Inc., 1950, p. 276.

halides shows that the greatest deviation from the angles observed for the hydrogen halides is 9° for fluorine; the others are 8° and 4° for chlorine and bromine respectively. Also the X----H distances in the 1-halo-2-phenylnaphthalenes compare favorably with the hydrogen bond distances of the hydrogen halides. The data indicates that the geometry of the C-X----H grouping in the 1-halo-2-phenylnaphthalenes is near the ideal geometry for the formation of a strong hydrogen-halogen attraction. The strength of this attraction will therefore be near the maximum for the partial negative charge on the halogen and partial positive charge on the hydrogen.

One of the important contributions to the energy of a hydrogen bond is a dipole-dipole type of interaction. This sytem would not be expected to exhibit the usual behavior of a dipole-dipole interaction, because the dipoles are not randomly oriented. The effectiveness of the interaction would be expected to be greater at 77°K than it would be at 25°C.

The room temperature and 77°K absorption spectra of 1-fluoro-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 11 and the spectroscopic data measured from these spectra are given in Table VI. The fluorescence and phosphorescence emission spectra measured in 3-MP at 77°K are shown in Figure 12 and the emission frequencies are given in Table VII.

The 0,0 band of the $^1L_b \leftarrow {}^1A$ transition in 1-fluoro-2-phenylnaphthalene measured in 3-MP at 77°K is observed at 30,490 $cm.^{-1}$ and is red-shifted 520 $cm.^{-1}$ relative to that of 2-phenylnaphthalene

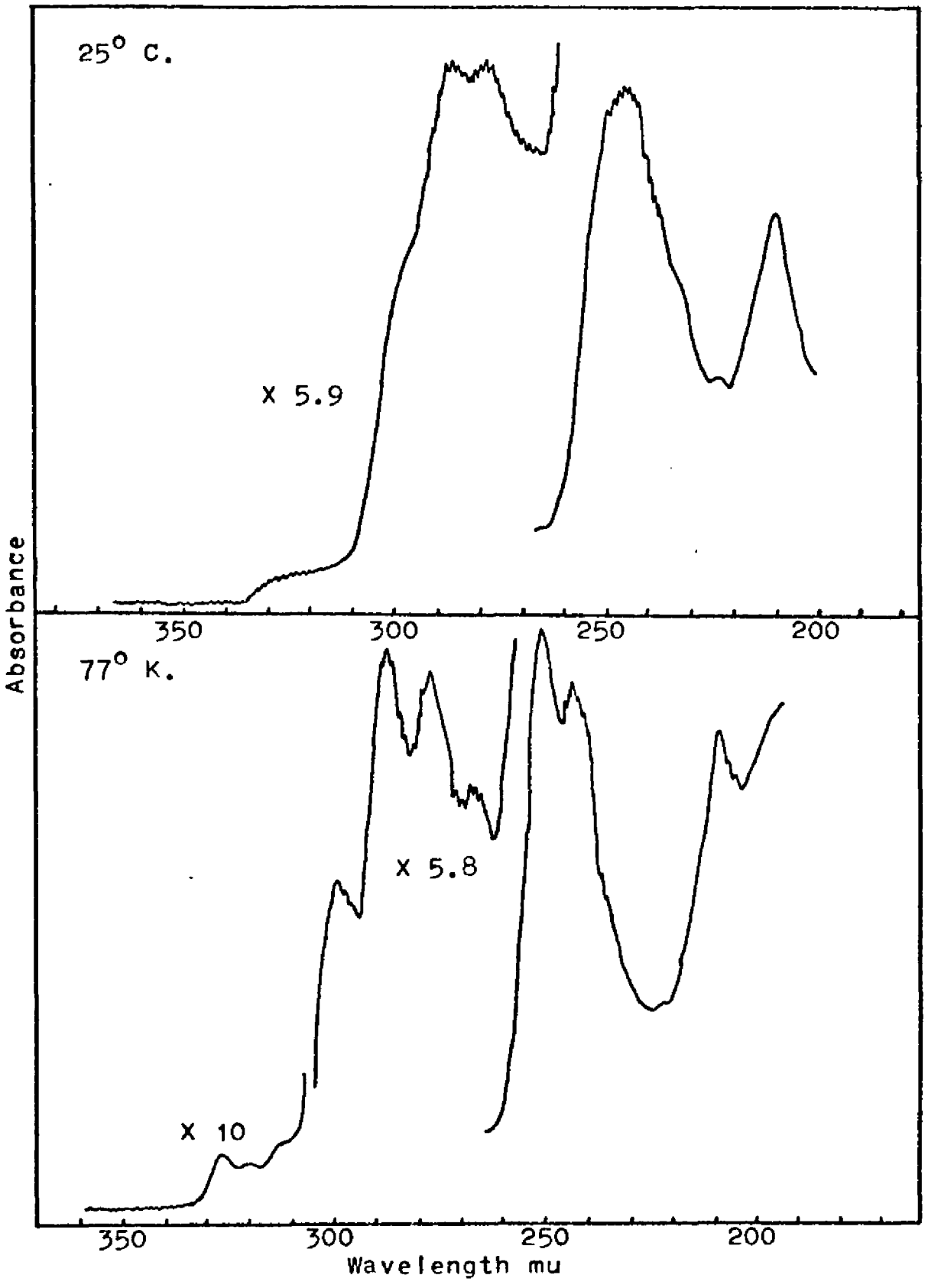


FIGURE 11. Room Temperature and 77° K. Absorption of 1-fluoro-2-phenylnaphthalene in Hydrocarbon

TABLE VI

Absorption Frequencies and Extinction Coefficients
of 1-Fluoro-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
3250	30,769	6.57×10^{2}
2850	35,088	1.14×10^{4}
2450	40,816	6.49×10^{4}
2120	47,170	4.60×10^{4}

77°K in 3-MP IP

A	Cm.$^{-1}$	$\Delta \nu$
3280	30,488	0
3200	31,250	762
3125	32,000	1512
3010	33,223	0
2890	34,602	1379
2780	35,971	2748
2680	37,313	4090
2530	39,526	0
2460	40,650	1124
2115	47,281	0

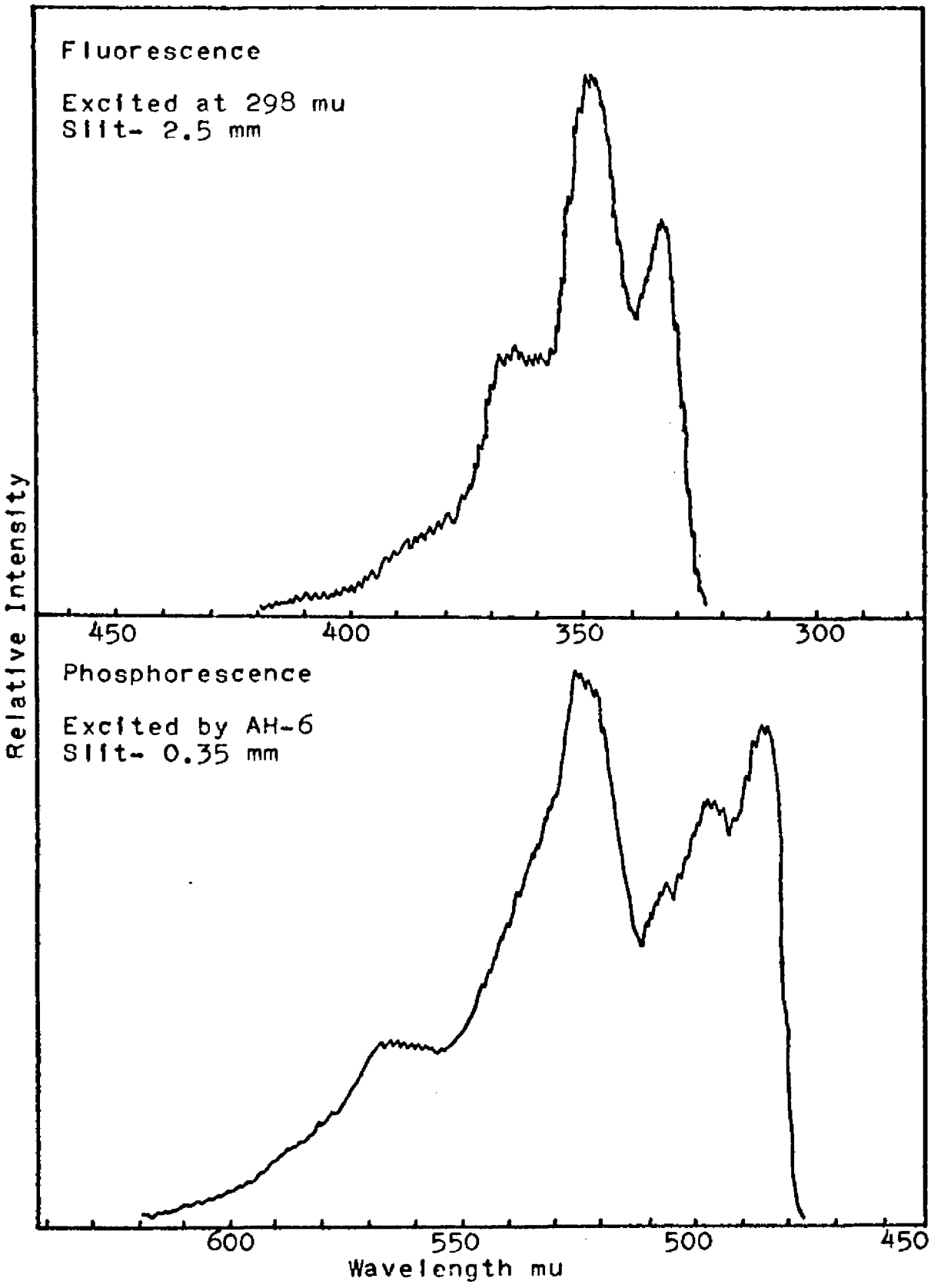


FIGURE 12. 77° K. Fluorescence and Phosphorescence of 1-fluoro-2-phenylnaphthalene in 3-methylpentane

TABLE VII

Emission Frequencies of 1-Fluoro-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta\nu$
3320	30,120	0
3480	28,736	1384
3660	27,322	2798
3860	25,907	4213

Phosphorescence

A	Cm.$^{-1}$	$\Delta\nu$
4860	20,576	0
4950	20,202	374
5030	19,881	695
5230	19,120	1456
5650	17,699	2907

measured under the same conditions. The red shift is much less than the shift observed between non-planar and planar 2-phenylnaphthalene (1770 cm.$^{-1}$) and indicates that 1-fluoro-2-phenylnaphthalene does not exist in the planar configuration in the equilibrium ground state. However, the 0,0 band observed at 30,120 cm.$^{-1}$ in the fluorescence emission of 1-fluoro-2-phenylnaphthalene is red shifted only 370 cm.$^{-1}$ from that observed in absorption. In terms of the arguments presented for 2-phenylnaphthalene this indicates that the equilibrium ground state of 1-fluoro-2-phenylnaphthalene, is planar or very nearly planar.

The data appear to be in direct conflict, but are interpretable in terms of the inductive effect of the fluorine atom on the pi electrons. The inductive effect stabilizes the pi cloud and for non-alternate molecules the stabilization differs between ground and excited states. If the stabilization is greater for the ground state than for the excited state, a blue shift is observed relative to the case in which the inductive effect is absent. Blue shifts of this type are frequently observed for non-alternate hydrocarbons.[60,61,62] The red-shift of 1-fluoro-2-phenylnaphthalene relative to that of non-planar 2-phenylnaphthalene is attributed to a planar configuration of 1-fluoro-2-phenylnaphthalene for the equilibrium ground state in solution at 77°K. The blue-shift

---

[60] P. A. Plattner and E. Heibronner, Helv. Chim. Acta., 31, 1948, p. 804.

[61] P. A. Plattner, Helv. Chim. Acta. 24, 1941, p. 283E.

[62] P. A. Plattner and E. Heilbronner, Helv. Chim. Acta. 30, 1947, p. 910.

relative to planar 2-phenylnaphthalene is attributed to the inductive effect of the fluorine atom. If the latter presumption is correct, the $^1L_b \leftarrow {}^1A$ transition observed for 1-chloro-2-phenylnaphthalene should be considerably red-shifted because of the decrease in the inductive effect.

Both the absorption spectrum and emission spectrum of 1-fluoro-2-phenylnaphthalene show more structure than that observed in the case of 2-phenylnaphthalene or 2'-methyl-2-phenylnaphthalene. This increased structure indicates that the distribution of molecules over the angle between rings is a narrow distribution and that the phenyl and naphthyl rings are more firmly attached. Although this data is qualitative, it is strong evidence that a deeper minimum exists in the zero-point energy curve in the case of 1-fluoro-2-phenylnaphthalene and that this minimum corresponds to the planar configuration.

There are some rather dramatic changes that occur in the $^1B_b \leftarrow {}^1A$ transition of 1-fluoro-2-phenylnaphthalene as the temperature is decreased from room temperature to 77°K. There is a significant increase in the vibrational structure in the low temperature spectrum just as in the first two transitions. There is also observed a red-shift and a narrowing of the $^1B_b \leftarrow {}^1A$ transition at 77°K compared to that at room temperature. The amount of red-shift cannot be determined accurately because of the lack of vibrational structure at room temperature. The spectral changes observed with change in temperature are again indicative

of a distribution of molecules over the angle between rings. The distribution is apparently much narrower at 77°K, a temperature at which the hydrogen-fluorine attractive forces become more important. These forces would tend to distribute a larger fraction of the molecules near the planar configuration in the equilibrium ground state. The position of the $^1B_b \leftarrow {}^1A$ transition in 1-fluoro-2-phenylnaphthalene is blue-shifted by 310 cm.$^{-1}$ compared with that of 2-phenylnaphthalene. It is difficult to rationalize such a shift; however, this may be due to the inductive effect of the fluorine atom.

The $^1C_b \leftarrow {}^1A$ transition in the room temperature spectrum of 1-fluoro-2-phenylnaphthalene occurs at exactly the same frequency as that in 2-phenylnaphthalene and in addition there was essentially no change or changing from 25°C to 77°K.

The room temperature and 77°K absorption spectra of 1-chloro-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 13 and the spectroscopic data are given in Table VIII. The fluorescence and phosphorescence emissions in 3-MP at 77°K are shown in Figure 14 and the emission frequencies are given in Table IX.

The 0,0 band of the $^1L_b \leftarrow {}^1A$ transition of 1-chloro-2-phenylnaphthalene in 3-MPIP at 77°K is observed at 29,760 cm.$^{-1}$ and is red-shifted 1,250 cm.$^{-1}$ relative to that of 2-phenylnaphthelen and 730 cm.$^{-1}$ relative to that of 1-fluoro-2-phenylnaphthalene. The energy difference between the 0,0 band measured in absorption and in fluorescence emission is 350 cm.$^{-1}$. The mirror image relationship between absorption and emission indicate that the equilibrium excited

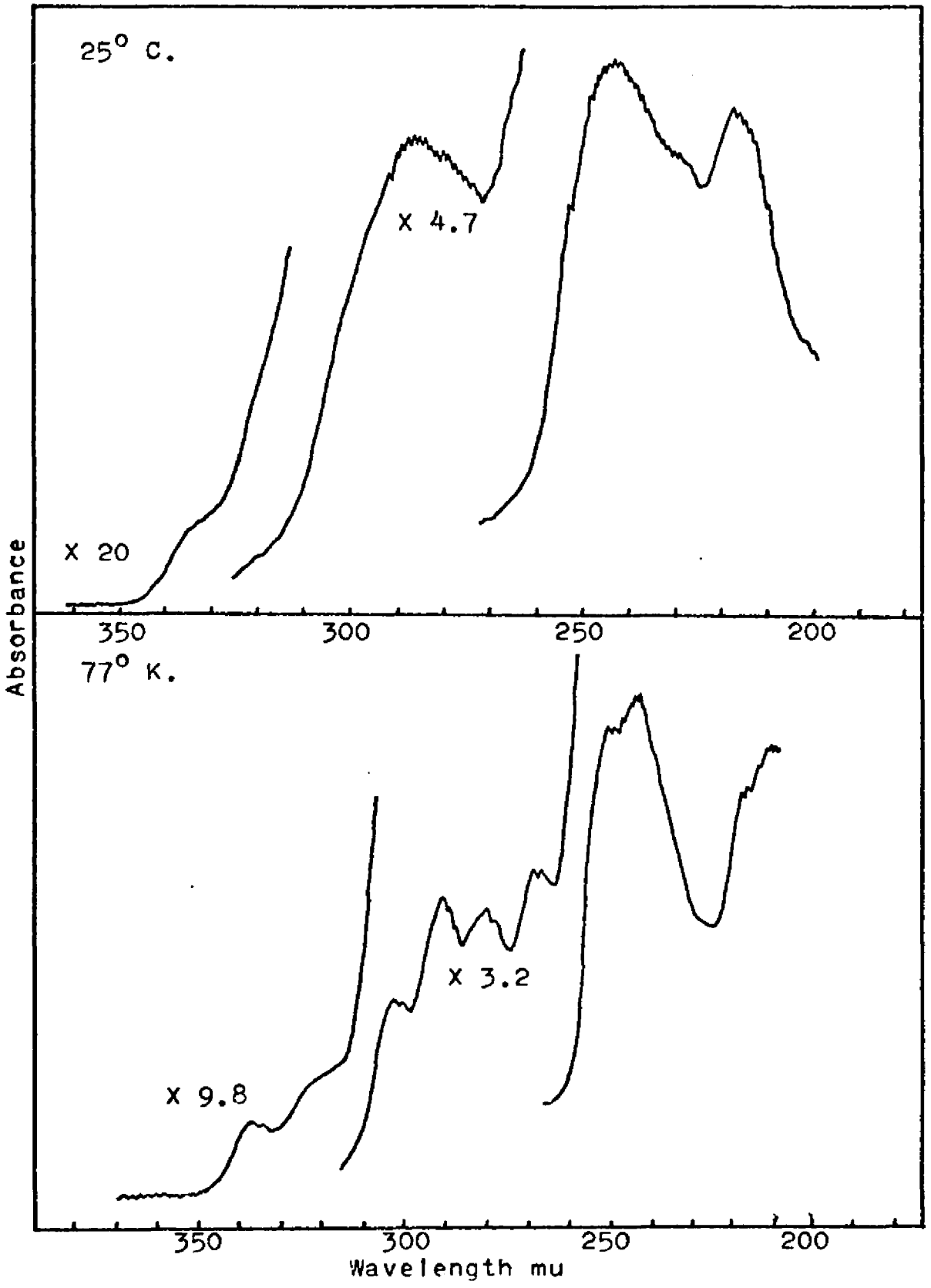


FIGURE 13. Room Temperature and 77° K. Absorption of 1-chloro-2-phenylnaphthalene in Hydrocarbon

TABLE VIII

Absorption Frequencies and Extinction Coefficients
of 1-Chloro-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
3300	30,303	3.88×10^{2}
2870	34,843	7.93×10^{3}
2430	41,152	4.26×10^{4}
2300	43,478	3.52×10^{4}
2180	45,871	3.91×10^{4}

77°K in 3-MPIP

A	Cm.$^{-1}$	$\Delta \nu$
3360	29,762	0
3210	31,153	1391
3030	33,003	0
2910	34,364	1361
2800	35,714	2711
2695	37,106	4103
2520	39,682	0
2450	40,816	1144
2180	45,871	0

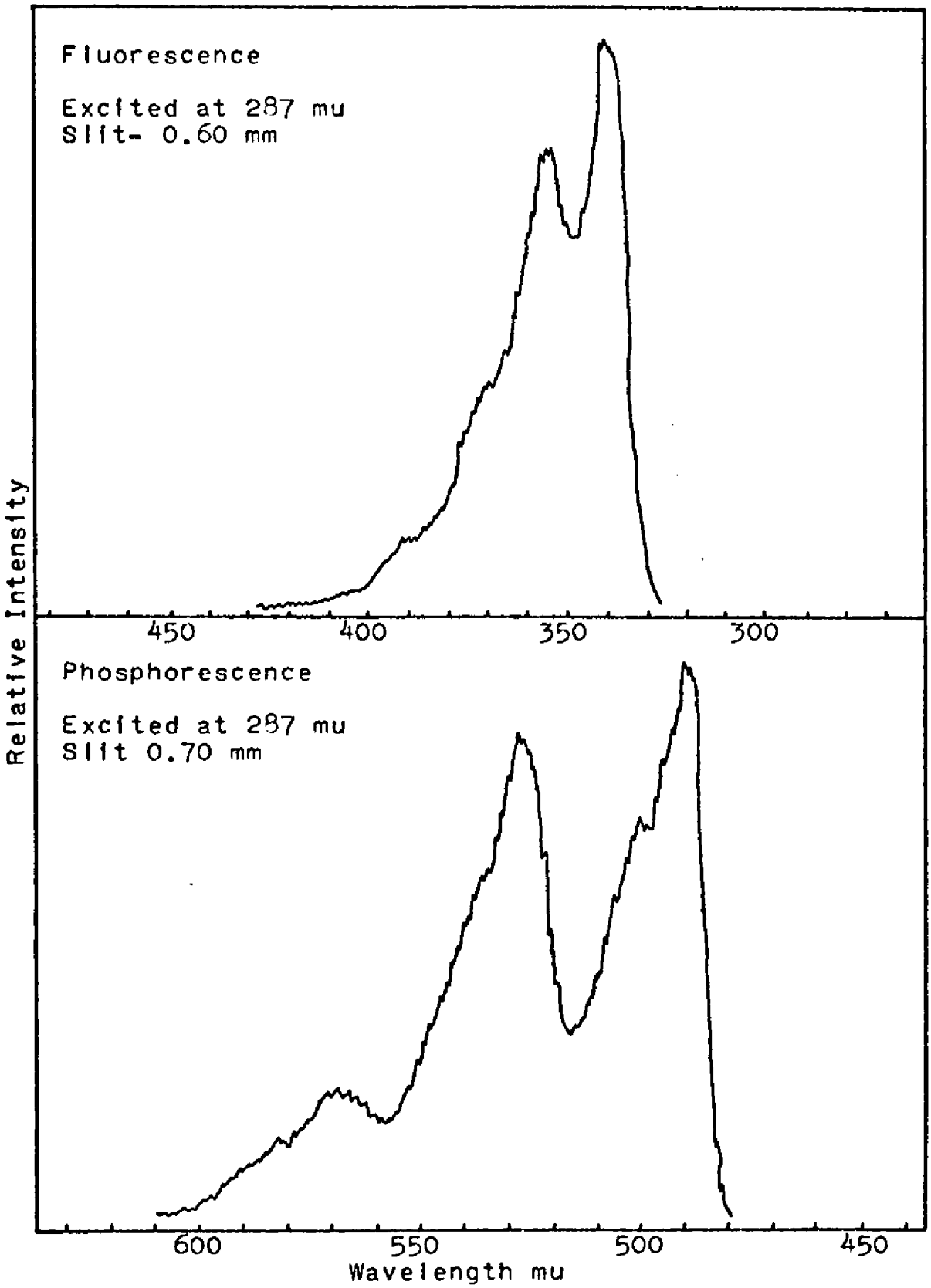


FIGURE 14. 77° K. Fluorescence and Phosphorescence of 1-chloro-2-phenylnaphthalene in 3-methylpentane

TABLE IX

Emission Frequencies of 1-Chloro-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3400	29,412	0
3565	28,050	1360
3750	26,667	2745
3950	25,316	4096

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
4910	20,367	0
5010	19,960	407
5280	18,939	1428
5710	17,513	2854

state and equilibrium ground state have essentially the same configuration. The exceptionally large red-shift relative to 1-fluoro-2-phenylnaphthalene (730 $cm.^{-1}$) supports the interpretation that an inductive effect at the 1-position in 2-phenylnaphthalene results in a blue shift in the $^1L_b \leftarrow {}^1A$ transition.

The fluorescence emission spectrum of 1-chloro-2-phenylnaphthalene shows considerable structure and again indicates that the emission is from a narrow distribution of molecules about the planar configuration. The structure of the emission is in direct conflict with the lack of structure observed in absorption. This difference in structure between absorption and emission has been faintly observed in the previously discussed systems but the difference is magnified in this case. In the case of 1-chloro-2-phenylnaphthalene the zero-point energy curve has a minimum corresponding to the planar configuration but the potential well is very shallow and therefore the molecular distribution as a function of the angle between the rings is very broad. Comparison between the room temperature absorption of 1-chloro-2-phenylnaphthalene and that of 1-fluoro-2-phenylnaphthalene shows that the 1-chloro-2-phenylnaphthalene spectrum is much broader (especially in the sensitive $^1B_b \leftarrow {}^1A$ transition) and has lower extinction coefficients for all the bands. This lack of structure is due to the superposition of many configurations and the observed decrease in extinction coefficients is due to effective lower concentrations of each species. Thus the 1-fluoro compound has a deeper potential well, which may be attributed to a greater attraction between the fluorine and 2'-hydrogen atom.

Comparison of the $^1B_b \leftarrow {}^1A$ transition of 1-chloro-2-phenylnaphthalene at room temperature with that at 77°K again reveals an increase in structure and narrowing of the transition at low temperature. Similar changes were observed in 1-fluoro-2-phenylnaphthalene and were more pronounced than those observed in the case of the 1-chloro compound. This again indicates that a distribution over many configuration at room temperature has been narrowed at 77°K in a manner consistent with a Boltzmann distribution. This too indicates an attraction between the chlorine and 2'-hydrogen atoms. As in the case of 1-fluoro-2-phenylnaphthalene, the $^1B_b \leftarrow {}^1A$ transition of 1-chloro-2-phenylnaphthalene at 77°K is observed to blue-shift 480 $cm.^{-1}$ compared with that of 2-phenylnaphthalene.

The $^1C_b \leftarrow {}^1A$ transition in 1-chloro-2-phenylnaphthalene is estimated to occur at 45,870 $cm.^{-1}$ (red-shifted 1300 $cm.^{-1}$ over that of 2-phenylnaphthalene) at room temperature and also at 77°K. This frequency is somewhat uncertain because there is severe overlap of the broad $^1B_b \leftarrow {}^1A$ transition at room temperature and poor resolution in the 77°K spectrum.

The room temperature and 77°K absorption spectra of 1-bromo-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 15 and the spectroscopic data are given in Table X. The fluorescence and phosphorescence emissions of solution in 3-MP at 77°K are shown in Figure 16 and the emission frequencies are given in Table XI.

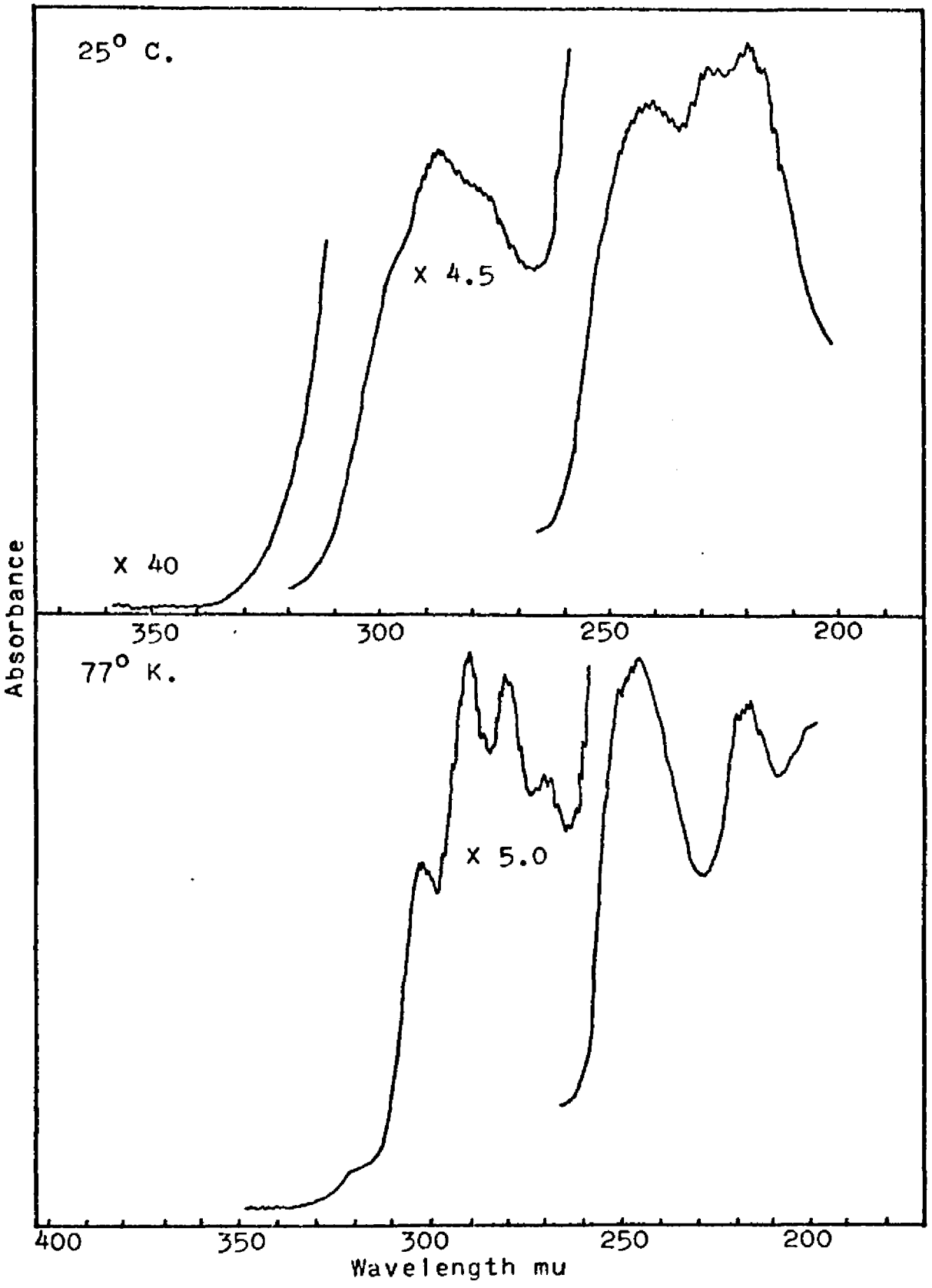


FIGURE 15. Room Temperature and 77° K. Absorption of 1-bromo-2-phenylnaphthalene in Hydrocarbon

TABLE X

Absorption Frequencies and Extinction Coefficients
of 1-Bromo-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
2870	34,843	7.90×10^3
2420	41,322	3.75×10^4
2280	43,860	4.35×10^4
2220	45,045	4.45×10^4

77°K in 3-MPIP

A	Cm.$^{-1}$	$\Delta \nu$
3370	29,674	0
3210	31,153	1479
3030	33,003	0
2920	34,246	1243
2815	35,524	2521
2720	36,765	3762
2520	39,683	0
2455	40,733	1050
2170	46,083	0

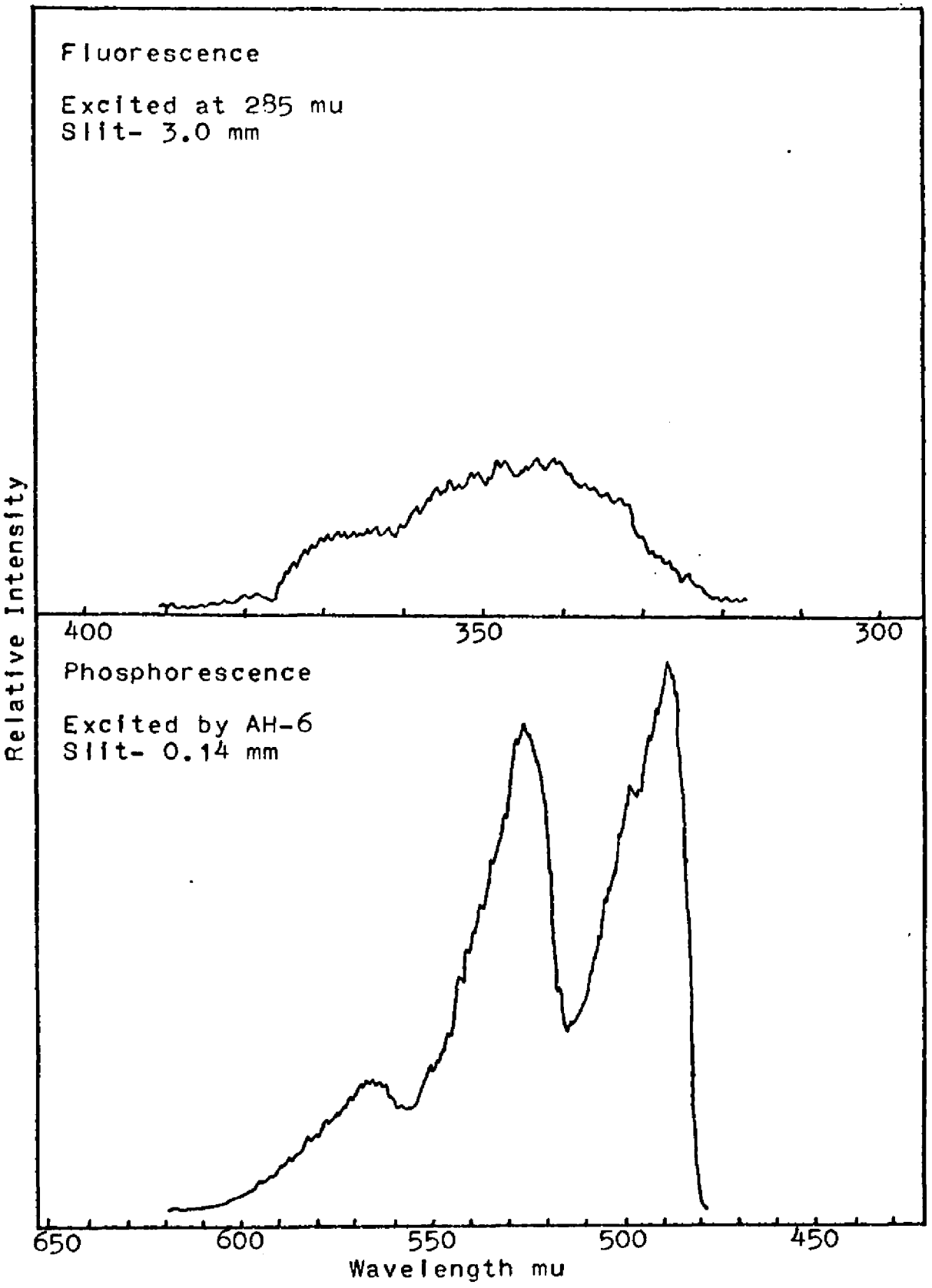


FIGURE 16. 77° K. Fluorescence and Phosphorescence of 1-bromo-2-phenylnaphthalene in 3-methylpentane

TABLE XI

Phosphorescence Frequencies of 1-Bromo-2-Phenylnaphthalene

A	Cm.$^{-1}$	$\Delta \nu$
4900	20,408	0
5000	20,000	408
5260	19,011	1397
5670	17,637	2771

The 0,0 band of the $^1L_b \leftarrow {}^1A$ transition of 1-bromo-2-phenylnaphthalene in 3-MPIP at 77°K is observed at 29,670 cm.$^{-1}$ and is red-shifted 1340 cm.$^{-1}$ relative to that of 2-phenylnaphthalene and 90 cm.$^{-1}$ relative to that of 1-chloro-2-phenylnaphthalene. This shift relative to 1-chloro-2-phenylnaphthalene again supports the interpretation that an inductive effect at the 1-position in 2-phenylnaphthalene results in a blue shift in the $^1L_b \leftarrow {}^1A$ transition. This same red-shift also tends to indicate that the zero-point energy curve for the equilibrium ground state of 1-bromo-2-phenylnaphthalene has a shallow minimum corresponding to the planar configuration. Because of the extremely low fluorescence intensity it is impossible to determine whether or not a mirror image relationship exists between the absorption and emission spectra of 1-bromo-2-phenylnaphthalene. Comparison of the room temperature absorption of 1-bromo-2-phenylnaphthalene and that of 1-chloro-2-phenylnaphthalene shows that the 1-bromo-2-phenylnaphthalene spectrum is much broader especially in the region of the $^1B_b \leftarrow {}^1A$ transition and there is a decrease in extinction coefficients for all bands. Again this loss of structure must be due to the superposition of the absorptions of many configurations.

As in the case of the corresponding 1-chloro derivative there is some increase in structure in the $^1B_b \leftarrow {}^1A$ transition of 1-bromo-2-phenylnaphthalene and a significant narrowing of the band when the temperature is decreased from room temperature to 77°K. This observation lends additional support to the interpretation that the room temperature absorption spectrum is a superposition of the absorption

of a distribution of many configurations. There is again evidence in the case of 1-bromo-2-phenylnaphthalene that the distribution is narrowed at 77°K in agreement with a Boltzmann distribution. This indicates that there is some attractive force between the bromine and 2'-hydrogen atoms.

The frequency of the $^1B_b \leftarrow {}^1A$ transition of 1-bromo-2-phenylnaphthalene at 77°K is exactly the same as that of 1-chloro-2-phenylnaphthalene (39,680 $cm.^{-1}$). This represents a 480 $cm.^{-1}$ blue-shift relative to 2-phenylnaphthalene. The $^1C_b \leftarrow {}^1A$ transition in the room temperature spectrum of 1-bromo-2-phenylnaphthalene cannot be accurately located because this transition and the broad $^1B_b \leftarrow {}^1A$ transition overlap. The frequency of the $^1C_b \leftarrow {}^1A$ transition at 77°K is 46,080 $cm.^{-1}$.

There are several experimental observations in the 1-halo-2-phenylnaphthalenes that lead to the conclusion that the geometric configuration of the equilibrium ground state at 77°K is either planar or very nearly so and at room temperature the equilibrium ground state consists of a distribution of configurations about the angle between the ring planes. Some of these observations are:

(a) Substitution of a halogen in the 1-position of 2-phenylnaphthalene has little or no effect on the frequency of the $^1L_a \leftarrow {}^1A$ transition but noticibly red-shifts the $^1L_b \leftarrow {}^1A$ transition.

(b) The extinction coefficients of the maxima in the $^1L_a \leftarrow {}^1A$ transitions of the 1-halonaphthalenes have been observed[63] to

---

[63] J. Ferguson, J. Chem. Soc., (1954), p. 305.

increase continuously through the halogen series F, Cl and Br but in the 1-halo-2-phenylnaphthalenes there is a decrease in the extinction coefficient of all the bands at room temperature through the same series.

(c) The energies of the 0,0 bands of absorption and emission are much closer together in this series of compounds than are those of 2-phenylnaphthalene.

(d) The bond angles and distances are about ideal for the formation of a hydrogen bond between the 1-halogen and the 2'-hydrogen if the temperature is sufficiently low and sufficient charges exist on the halogen and hydrogen atoms.

(e) There is an unusually large increase in band structure in the 1-halo-2-phenylnaphthalenes as the temperature is lowered from room temperature to 77°K. There is also observed an appreciable red shift and narrowing of the $^1B_b \leftarrow {}^1A$ transition with decrease in temperature. This is indicative of a narrowing of the distribution of molecules about the angle between rings as the temperature decreases.

There has been observed in 2'-methyl-2-phenylnaphthalene, 1-chloro-2-phenylnaphthalene and 1-bromo-2-phenylnaphthalene a transition in the 2300 A. region of the room temperature absorption spectrum that essentially disappears at 77°K. There is also observed a significant red-shift in the $^1B_b \leftarrow {}^1A$ transition at low temperature. In the discussion of the 1-halo-2-phenylnaphthalenes the transition in the

2300 A. region has been considered to be simply a broadening of the $^1B_b \leftarrow {}^1A$ transition due to Boltzmann angular distribution of the molecules. This assignment can be justified by considering the consistency of such a distribution at room temperature and how it should change as the temperature is decreased to 77°K. The predicted shape of the $^1B_b \leftarrow {}^1A$ transitions as a function of temperature is shown in Figure 17. At all temperatures shown the $^1B_b \leftarrow {}^1A$ transition observed may be considered a sum of the $^1B_b \leftarrow {}^1A$ transitions of molecules with many different angular configurations, however, as the temperature decreases fewer and fewer of these configurations can be substantially populated. The upper limit of the distribution has been set at approximately 2300 A. (43,480 $cm.^{-1}$) corresponding to a molecule with the phenyl ring at 90° out-of-plane. This transition should occur at approximately the same frequency as that of a 2-alkyl substituted naphthalene. The lower limit has been set at approximately 2500 A. (40,000 $cm.^{-1}$) corresponding to the 77°K frequency of the $^1B_b \leftarrow {}^1A$ transition of 1-fluoro-2-phenylnaphthalene, which is believed to be planar. When the temperature is sufficiently high so that the system is classically excited, there should exist all transitions between these two limits. The combination of all such transitions at room temperature gives the appearance of a broad $^1B_b \leftarrow {}^1A$ and the high energy (out-of-plane) portion of spectrum combined with the low energy edge of the $^1C_b \leftarrow$ transition in the 1-halo-2-phenylnaphthalenes gives the appearance of a new transition at approximately 2300 A. One might postulate the existence of a

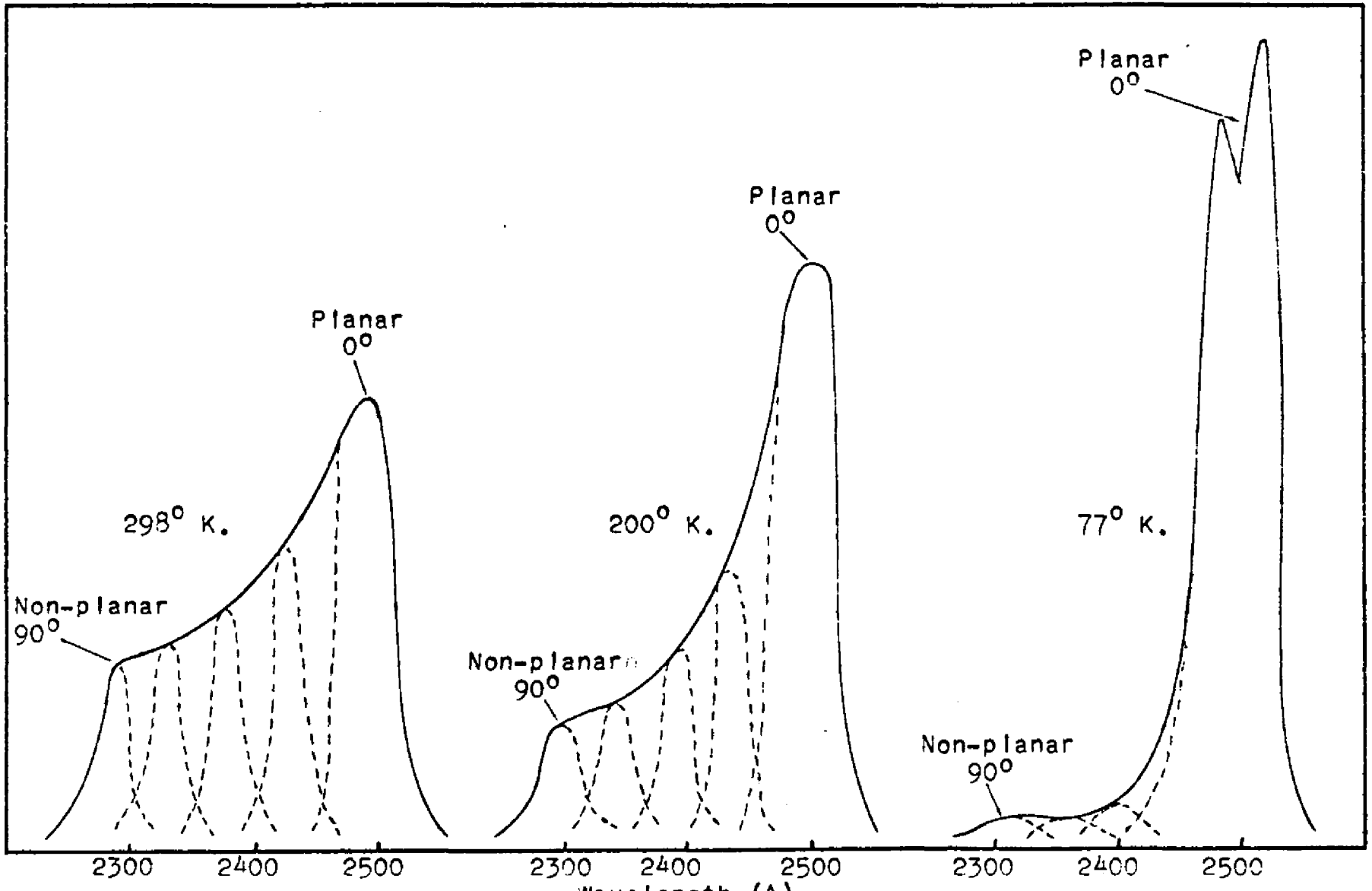


FIGURE 17. Distribution of $^1B_b \leftarrow {}^1A$ Transitions For 1-Halo-2-Phenylnaphthalenes As a Function of Temperature

shallow minimum in the room temperature zero-point energy curve at the 90° angle that would cause an intensification of the transition corresponding to the out of plane configuration. There is not sufficient experimental evidence to justify such a conclusion in the case of the 1-halo-2-phenylnaphthalenes.

It should be noted that a $^1B_b \leftarrow {}^1A$ transition corresponding to an out-of-plane configuration is not observed in 1-fluoro-2-phenylnaphthalene at room temperature. This observation provides additional evidence that the minimum in the zero-point energy curve corresponding to the planar configuration is deeper for 1-fluoro-2-phenylnaphthalene than for the other 1-halo-2-phenylnaphthalenes. Apparently a temperature higher than room temperature is necessary to appreciably populate those configurations with energies higher than the ones near the planar configuration.

Experimental evidence has been presented which indicates that the minimum in the zero-point energy curve for the 1-halo-2-phenylnaphthalenes at 77°K corresponds to a near planar configuration. At the 77°K temperature only the configurations near this potential minimum can be appreciably populated. Under these conditions the $^1B_b \leftarrow {}^1A$ transition has the narrow appearance of essentially a single planar configuration as shown in Figure 17 for the 77°K case. At some temperature intermediate between room temperature and 77°K there should be some population of the out-of-plane configurations but less than at room temperature. One would expect a distribution similar to that shown for 200°K (Figure 17) under these conditions.

The angular distribution explanation presented is consistent with the available experimental data for the 1-halo-2-phenylnaphthalenes, however, more experimental observations need to be carried out on changes in intensity of the $^1B_b \leftarrow {}^1A$ transitions as the temperature is varied from above room temperature to 77°K to determine whether or not the intensity changes correspond to a Boltzmann distribution.

E. Spectra of the 2'-Halo-2-Phenylnaphthalenes and 4'-Halo-2-Phenylnaphthalenes

In the 2'-halo-2-phenylnaphthalenes the geometry of the H----X-C group for the planar configuration should be very similar to that of the 1-halo-2-phenylnaphthalenes. There are, however, two non-equivalent planar configuration; one with the halogen adjacent to the 1-hydrogen and the other with the halogen adjacent to the 3-hydrogen of the naphthalene ring. Any attempt to establish which configuration is the more stable would be based upon presumptive interpretation of data. Considering the small energies involved, the two planar configurations probably have nearly equal zero-point energies. In addition the zero-point energy curves of the 1-halo-2-phenylnaphthalenes and those of the 2'-halo-2-phenylnaphthalene should be very similar because the resonance stabilization, charge repulsions and charge attractions should be essentially the same between the two molecules. There are indications that the hydrogen-halogen attraction would be slightly less for the 2'-halo-2-phenylnaphthalenes, since the charge

on the halogen should be slightly less when it is attached to the phenyl ring. The absorption and emission spectroscopy of the 2'-halo-2-phenylnaphthalenes does not confirm the contention that the zero-point energy curves are similar and in fact indicates the zero-point energy curves for the 2'-halo compounds are very different from the 1-halo-2-phenylnaphthalenes.

The 4'-halo-2-phenylnaphthalenes were included in order to study the heavy atom effect and the effect of extending conjugation by a halogen in the 4'-position.

The room temperature and 77°K absorption spectra of 2'-fluoro-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 18 and the corresponding spectroscopic data are given in Table XII. The fluorescence and phosphorescence emissions in 3-MP at 77°K are shown in Figure 19 and the emission frequencies are given in Table XIII.

The absorption spectrum of 2'-fluoro-2-phenylnaphthalene shows considerably less structure than that of 1-fluoro-2-phenylnaphthalene. This indicates that there is a broad distribution of configurations with respect to the angle between rings for the former compound even at 77°K. The $^1L_b \leftarrow {}^1A$ transition is so weak and diffuse that the frequency of the 0,0 band cannot be accurately measured, but is estimated to be near 31,000 $cm.^{-1}$ in rigid glassy 3-MPIP and is very near that of 2-phenylnaphthalene (31,010 $cm.^{-1}$). In the crystal absorption spectrum at room temperature no longer wavelength bands were observed as they were in 2-phenylnaphthalene. However, very

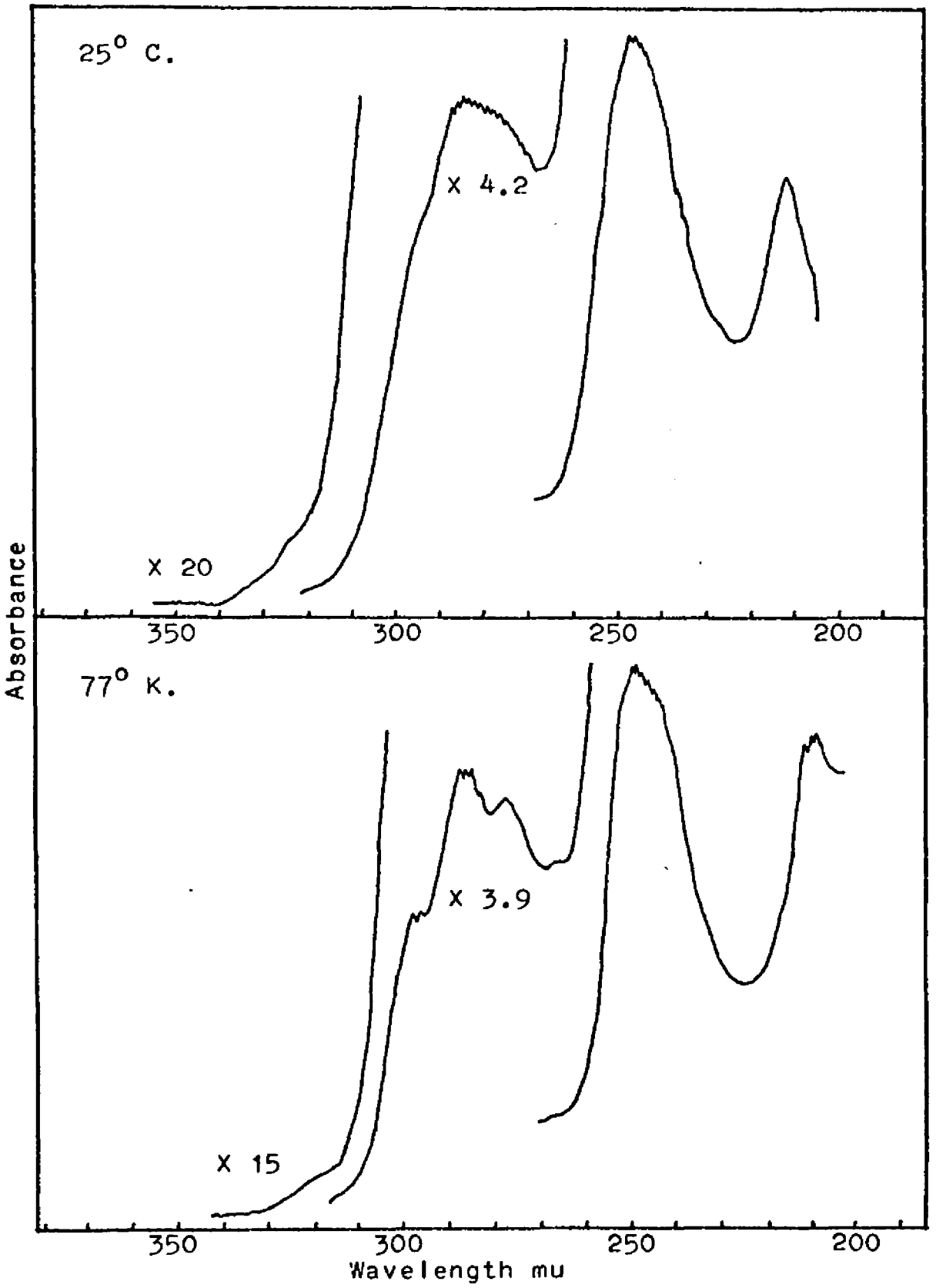


FIGURE 18. Room Temperature and 77° K. Absorption of 2'-fluoro-2-phenylnaphthalene in Hydrocarbon

TABLE XII

Absorption Frequencies and Extinction Coefficients
of 2'-Fluoro-2-Phenylnaphthalene

25°C in 3-MP

A	$Cm.^{-1}$	ϵ(liter/mole cm.)
3240	30,864	3.50×10^2
2870	34,843	1.40×10^4
2470	41,486	6.15×10^4
2120	47,170	4.85×10^4

77°K in 3-MP1P

A	$Cm.^{-1}$	$\Delta \nu$
3220	31,056	0
3000	33,333	0
2885	34,662	1329
2775	36,036	2703
2675	37,383	4050
2510	39,841	0
2440	40,984	1143
2110	47,393	0

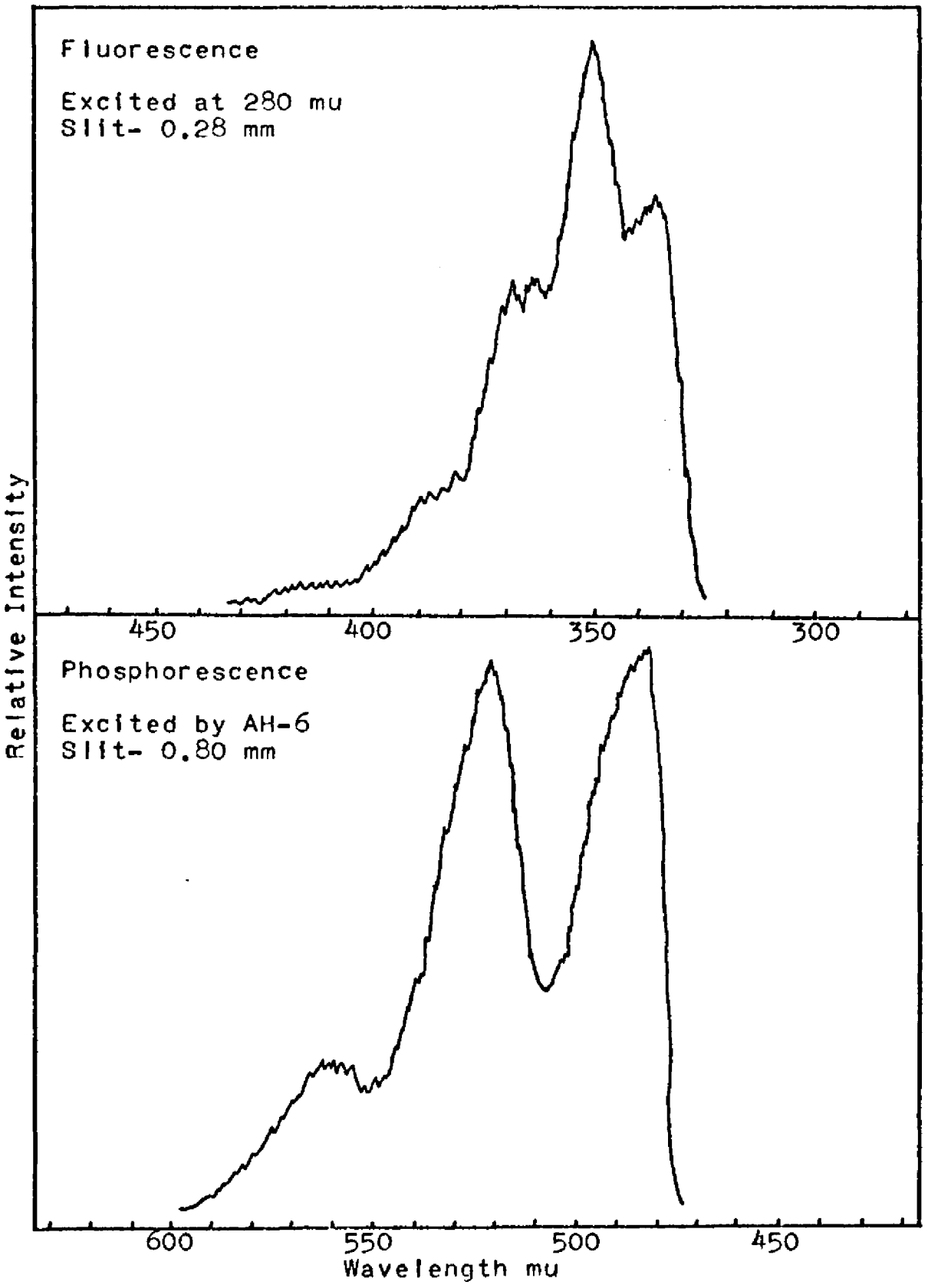


FIGURE 19. 77° K. Fluorescence and Phosphorescence of 2'-fluoro-2-phenylnaphthalene in 3-methylpentane

TABLE XIII

Emission Frequencies of 2'-Fluoro-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3325	30,075	0
3360	29,762	313
3510	28,490	1585
3675	27,211	2864
3885	25,940	4135

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
4840	20,661	0
5200	19,231	1430
5610	17,825	2836

low intensity bands do appear at approximately 3420 A. (29,240 cm.$^{-1}$) in a saturated rigid glassy solution and again are very near those of crystalline 2-phenylnaphthalene (29,240 cm.$^{-1}$). The data indicate that 2'-fluoro-2-phenylnaphthalene is distributed about a non-planar equilibrium ground state in rigid glassy solution and that the molecule is non-planar in the crystal at room temperature but attains the planar configuration in the crystal grown near 77°K.

The 0,0 band of the fluorescence emission is observed at 30,075 cm.$^{-1}$, very near that of 1-fluoro-2-phenylnaphthalene (30,120 cm.$^{-1}$), but unlike 1-fluoro-2-phenylnaphthalene the emission can not be from a planar species because the emission is 835 cm.$^{-1}$ blue shifted from the planar absorption. The fluorescence emission from 2'-fluoro-2-phenylnaphthalene is apparently an emission from a non-planar configuration. Previously the 2'-methyl-2-phenylnaphthalene emission was assigned as a non-planar emission. Comparisons between the fluorescence emissions of 2'-methyl and 2'-fluoro and those of the other 2'-phenylnaphthalenes shows that the Franck-Condon band contour for 2'-methyl and 2'-fluoro-2-phenylnaphthalene are very similar (the 0,0 band is less intense than the 0,1 band) but differ significantly from the band contour of the emissions assigned to the planar configuration (the 0,0 band has the same or greater intensity than that of the 0,1 band and a normal progression follows). The case of 1-fluoro-2-phenylnaphthalene is an exception, however, In addition, the band contour associated with emissions from the non-planar configuration are similar to those of 2-alkyl naphthalenes. These differences in

band shape strongly support the contention that the geometry of the equilibrium excited state of 2'-fluoro-2-phenylnaphthalene is non-planar.

The vibrational frequencies of the excited state could not be determined because of lack of structure in the $^1L_b \leftarrow {}^1A$ transition. It is, therefore, impossible to compare vibrational frequencies of the ground and excited states of 2'-fluoro-2-phenylnaphthalene.

The room temperature and 77°K absorption spectra of 2'-chloro-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 20 and the corresponding spectral data is given in Table XIV. The fluorescence and phosphorescence emission spectra measured in 3-MP at 77°K are shown in Figure 21 and the corresponding emission frequencies are given in Table XV.

In the absorption spectrum of 2'-chloro-2-phenylnaphthalene the $^1L_b \leftarrow {}^1A$ transition is very weak and diffuse similar to that observed for 2'-methyl and 2'-fluoro-2-phenylnaphthalene. The 0,0 band of the fluorescence is shifted only 310 $cm.^{-1}$ from the 0,0 band of the first absorption transition. These data indicates that the equilibrium ground state is non-planar and that the equilibrium excited state has a very similar configuration. The vibrational frequency in the ground state (1380 $cm.^{-1}$) compared to 1030 $cm.^{-1}$ in the excited state is further indication that the geometry of the ground state is similar to that in the excited state.

In the room temperature absorption spectrum there is evidence that the $^1C_b \leftarrow {}^1A$ transition has gained intensity relative to the

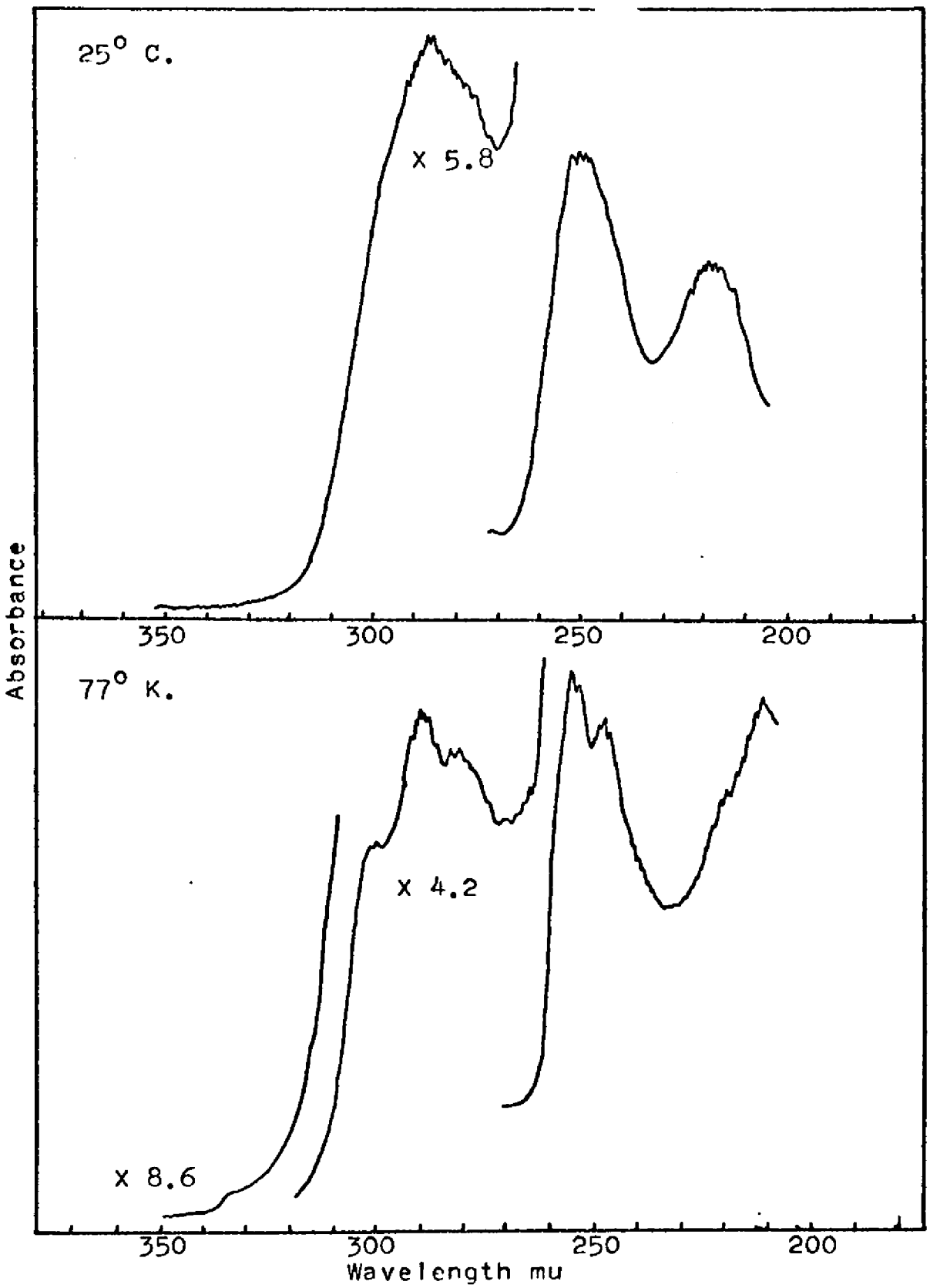


FIGURE 20. Room Temperature and 77° K. Absorption of 2'-chloro-2-phenylnaphthalene in Hydrocarbon

TABLE XIV

Absorption Frequencies and Extinction Coefficients
of 2'-Chloro-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
3250	30,769	4.80×10^{2}
2880	34,722	1.14×10^{4}
2520	39,683	4.88×10^{4}
2200	45,455	3.72×10^{4}
2170	46,083	3.84×10^{4}

77°K in 3-MPIP

A	Cm.$^{-1}$	$\Delta \nu$
3320	30,120	0
3210	31,153	1033
3025	33,058	0
2910	34,364	1306
2800	35,714	2656
2700	37,037	3979
2560	39,063	0
2490	40,161	1098
2200	45,455	0
2125	47,059	0

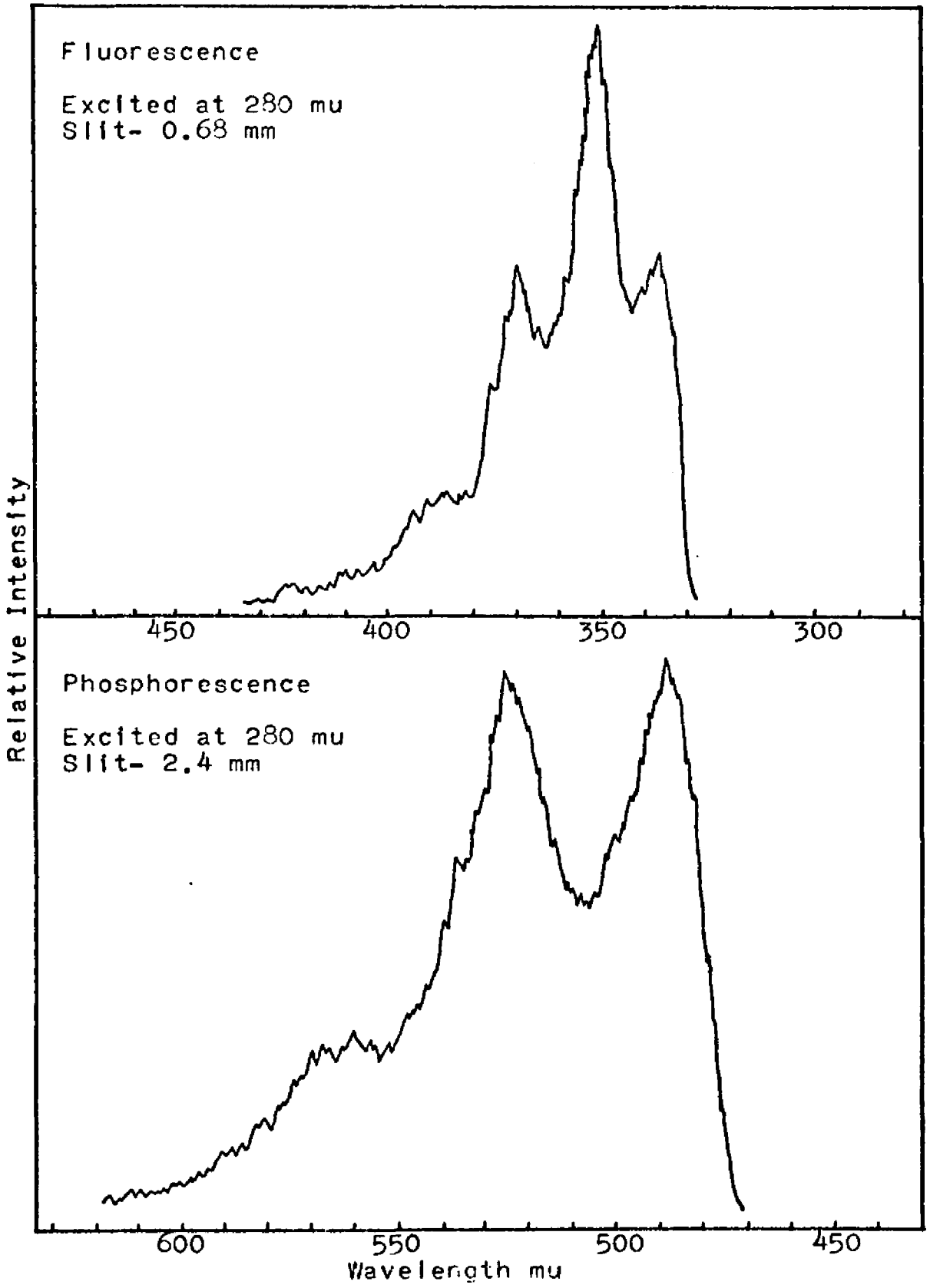


FIGURE 21. 77° K. Fluorescence and Phosphorescence of 2'-chloro-2-phenylnaphthalene in 3-methylpentane

TABLE XV

Emission Frequencies of 2'-Chloro-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3355	29,806	0
3520	28,409	1397
2700	27,027	2779
3900	25,641	4165

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
4900	20,408	0
5255	19,029	1379
5670	17,637	2771

$^1B_b \leftarrow {}^1A$ transition. This effect was observed and discussed for the case of 1-bromo-2-phenylnaphthalene and was attributed to a broadening of the $^1B_b \leftarrow {}^1A$ transition. Unlike the case of 1-bromo-2-phenylnaphthalene the transition, which is near 2200 A. in this case, does not disappear at 77°K but can still be observed as a shoulder on the $^1C_b \leftarrow {}^1A$ transition. If this band at 2200 A. is interpreted to be the $^1B_b \leftarrow {}^1A$ transition for the naphthalene subsystem for the 90° (out-of-plane) configuration, there must be a minimum in the zero-point energy curve at 90 degrees. Thus, at 77°K the distribution of molecules with respect to the angle between rings would show a minimum at 90 degrees and a minimum at a smaller angle presumably close to but not equal to zero degrees. The zero-point energy at the smaller angle must be lower than that at 90 degrees since relative intensities indicate that there is a higher population of molecules in the lower angle configuration. This is discussed more fully under 2'-bromo-2-phenylnaphthalene, in which the effect is more pronounced.

The room temperature and 77°K absorption spectra of 2'-bromo-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 22 and the corresponding spectral data is given in Table XVI. The fluorescence and phosphorescence spectra measured in 3-MP at 77°K are shown in Figure 23 and the corresponding phosphorescence frequencies are given in Table XVII. Due to the extremely low intensity of the fluorescence emission it was impossible to accurately determine emission frequencies.

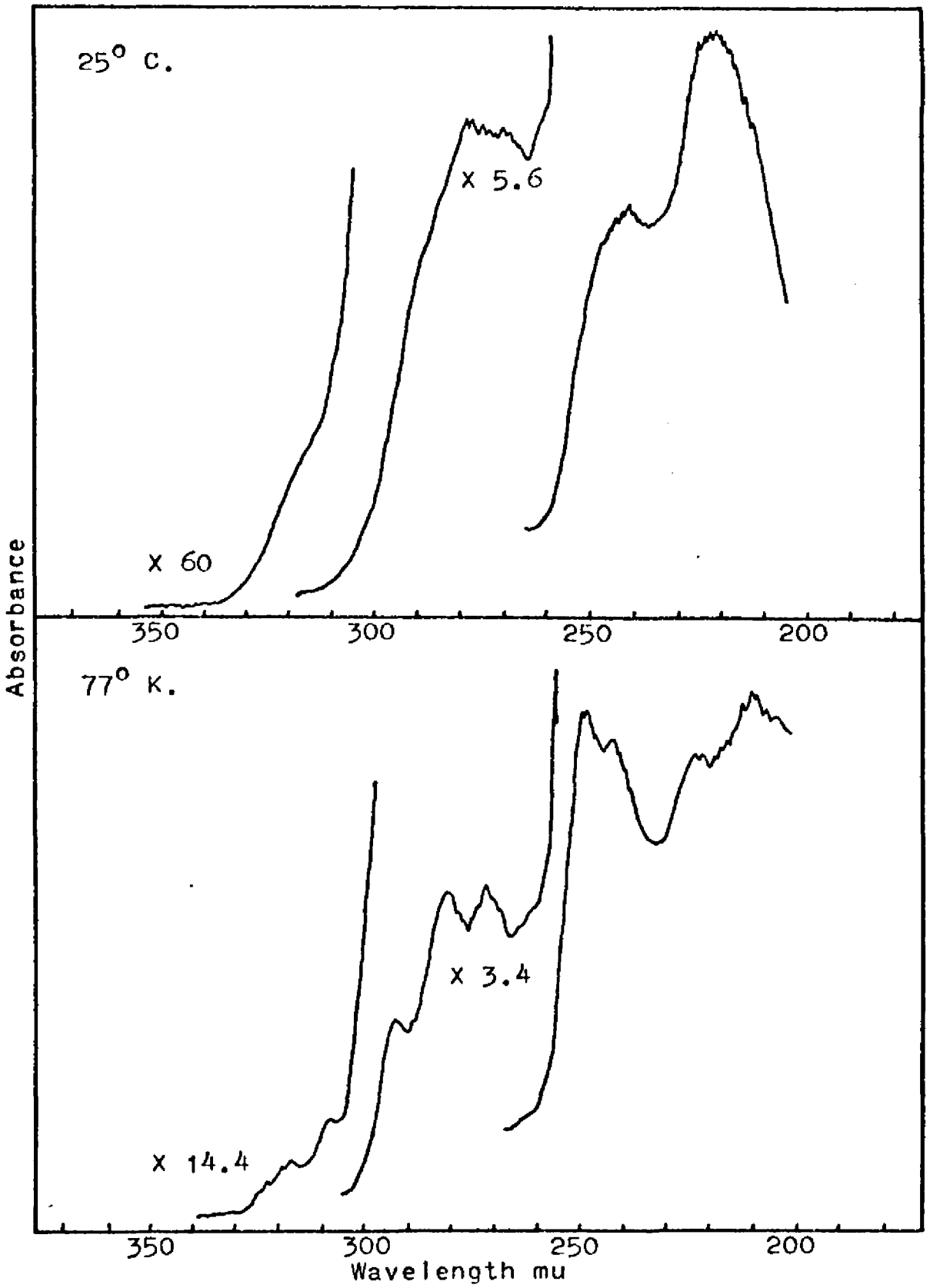


FIGURE 22. Room Temperature and 77° K. Absorption of 2'-bromo-2-phenylnaphthalene in Hydrocarbon

TABLE XVI

Absorption Frequencies and Extinction Coefficients
of 2'-Bromo-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
3125	32,000	4.0×10^2
2780	35,971	7.96×10^3
2420	41,322	3.56×10^4
2230	44,843	5.20×10^4

77°K in 3-MP|P

A	Cm.$^{-1}$	$\Delta \nu$
3220	31,056	0
3170	31,546	490
3080	32,467	1411
2930	34,130	0
2820	35,461	1331
2720	36,765	2635
2625	38,095	3965
2500	40,000	0
2430	41,152	1152
2250	44,170	0
2120	47,170	0

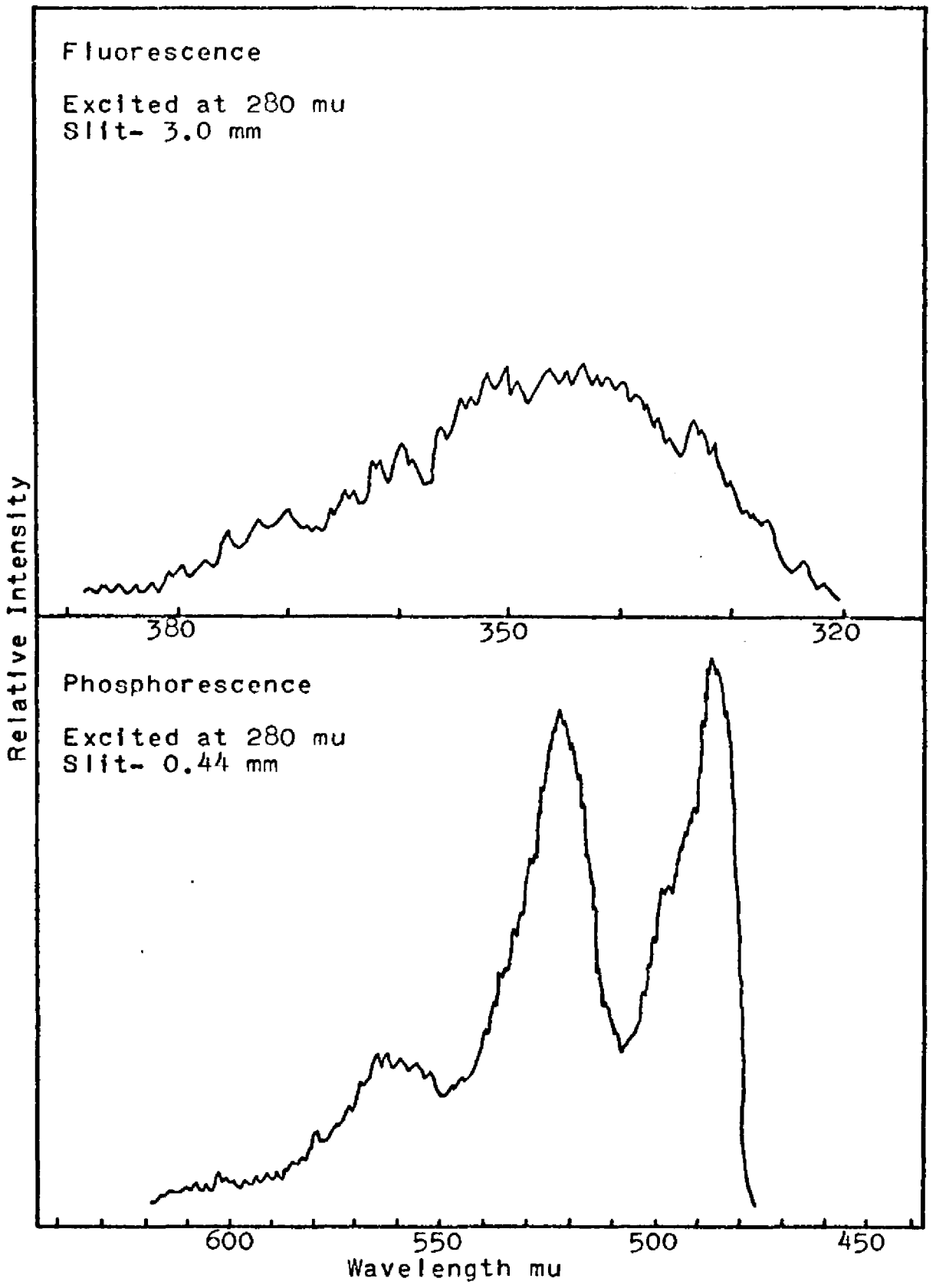


FIGURE 23. 77° K. Fluorescence and Phosphorescence of 2'-bromo-2-phenylnaphthalene in 3-methylpentane

TABLE XVII

Phosphorescence Frequencies of 2'-Bromo-2-Phenylnaphthalene

A	Cm.$^{-1}$	$\Delta \nu$
4865	20,555	0
4975	20,100	455
5225	19,139	1416
5640	17,730	2825

The absorption spectra of 2'-bromo-2-phenylnaphthalene show very significant differences when compared with those of the previous 2'-halo derivatives. The first three electronic transitions in the low temperature spectrum are blue-shifted approximately 1000 $cm.^{-1}$ compared with those of the 2'-chloro-derivative and the $^1L_b \leftarrow {}^1A$ transition, although still very weak shows considerable structure. In the room temperature spectrum the $^1C_b \leftarrow {}^1A$ region is considerably more intense than the $^1B_b \leftarrow {}^1A$ transition, which has lost considerable intensity, and at low temperature the $^1C_b \leftarrow {}^1A$ appears as two transitions. The effect is the same as that observed in the case of the 2'-chloro compound but it is much more pronounced. Again these data indicate that two minima exist in the zero-point energy curve and both are populated at 77°K. The enhancement of the transition at 44,170 $cm.^{-1}$ (previously assigned to be the $^1B_b \leftarrow {}^1A$ of the 90 degree configuration) indicates that the two minima have nearly equal energies, but the intensity of the $^1B_b \leftarrow {}^1A$ transition for the intermediate angle configuration indicates that the intermediate angle configuration is still the more highly populated. The blue shift relative to the position of the 2'-chloro-2-phenylnaphthalene indicates that the minimum in the zero-point energy curve corresponding to the intermediate angle configuration occurs at a larger angle for 2'-bromo-2-phenylnaphthalene.

The strong evidence that two predominant configurations exist at low temperature indicates that two fluorescences could possibly be observed at low temperature. Unfortunately the heavy atom effect produces such a high rate of intersystem crossing that the fluorescence

emission is extremely weak and could not be resolved with the Cary instrument. This predominate heavy atom effect also supports the interpretation that the 2'-halo compounds are non-planar and is discussed in section G.

The minimum at 90 degrees in the zero-point energy curve is not difficult to understand. The hydrogen-hydrogen interaction energy is very small and positive at 90 degrees; the hydrogen-halogen interaction energy is very small and probably negative at 90 degrees; the resonance stabilization energy is zero at 90 degrees. Thus these three terms add to essentially zero energy at 90 degrees. If there is any interaction which has a stabilizing effect at 90 degrees, then there should be a minimum in the zero-point energy curve at that angle. At the 90 degree configuration the halogens of the 1-halo-2-phenylnaphthalenes overlap the pi cloud of the phenyl ring; the hydrogens of the methyl group of 2'-methyl-2-phenylnaphthalene overlap the pi cloud of the naphthalene ring and the halogens of the 2'-halo-2-phenylnaphthalenes overlap the pi cloud of the naphthalene ring. Thus for the halogens a charge resonance interaction must be present and for the methyl group a hydrogen-pi cloud attraction must exist. All of these 90 degree interactions must be small in magnitude.

The spectroscopic data indicate that the hydrogen-halogen attraction is greater for the 1-halo derivatives than for the 2'-halo derivatives but that the halogen-pi cloud charge resonance interaction is greater for the 2'-halo derivatives in which the halogen is interacting with the naphthalene ring. Both of these

observations are consistent with the greater polarizability associated with the naphthalene ring. In addition the spectroscopic data indicate that the charge resonance interaction increases in the order; fluorine, chlorine, bromine.

The room temperature and 77°K absorption spectra of 4'-chloro-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 24 and the corresponding spectral data is given in Table XVIII. The fluorescence and phosphorescence spectra of 4'-chloro-2-phenylnaphthalene measured at 77°K in 3-MP is shown in Figure 25 and the emission frequencies are given in Table XIX.

In the room temperature absorption spectrum of 4'-chloro-2-phenylnaphthalene the $^1L_b \leftarrow {}^1A$ transition is hidden by the more intense $^1L_a \leftarrow {}^1A$ transition. At high concentrations there is evidence for an absorption near 30,800 $cm.^{-1}$, which is interpreted to be the $^1L_b \leftarrow {}^1A$ transition. The $^1L_a \leftarrow {}^1A$, $^1B_b \leftarrow {}^1A$ and $^1C_b \leftarrow {}^1A$ transitions are essentially the same as those observed in 2-phenylnaphthalene. There is no evidence for a 90 degree configuration in the $^1B_b \leftarrow {}^1A$ transition and this result is consistent with the interpretation that only 2'-substitution can provide the stabilization required to populate the 90 degree configurations. At low temperature and high concentration the $^1L_b \leftarrow {}^1A$ transition red shifts (1560 $cm.^{-1}$) to 29,240 $cm.^{-1}$. Since no absorption was observed in this region at room temperature, this absorption cannot correspond to a stable configuration for the molecule in solution. It is probable that the first weak absorption observed at low temperature is due to dimers and higher aggregates

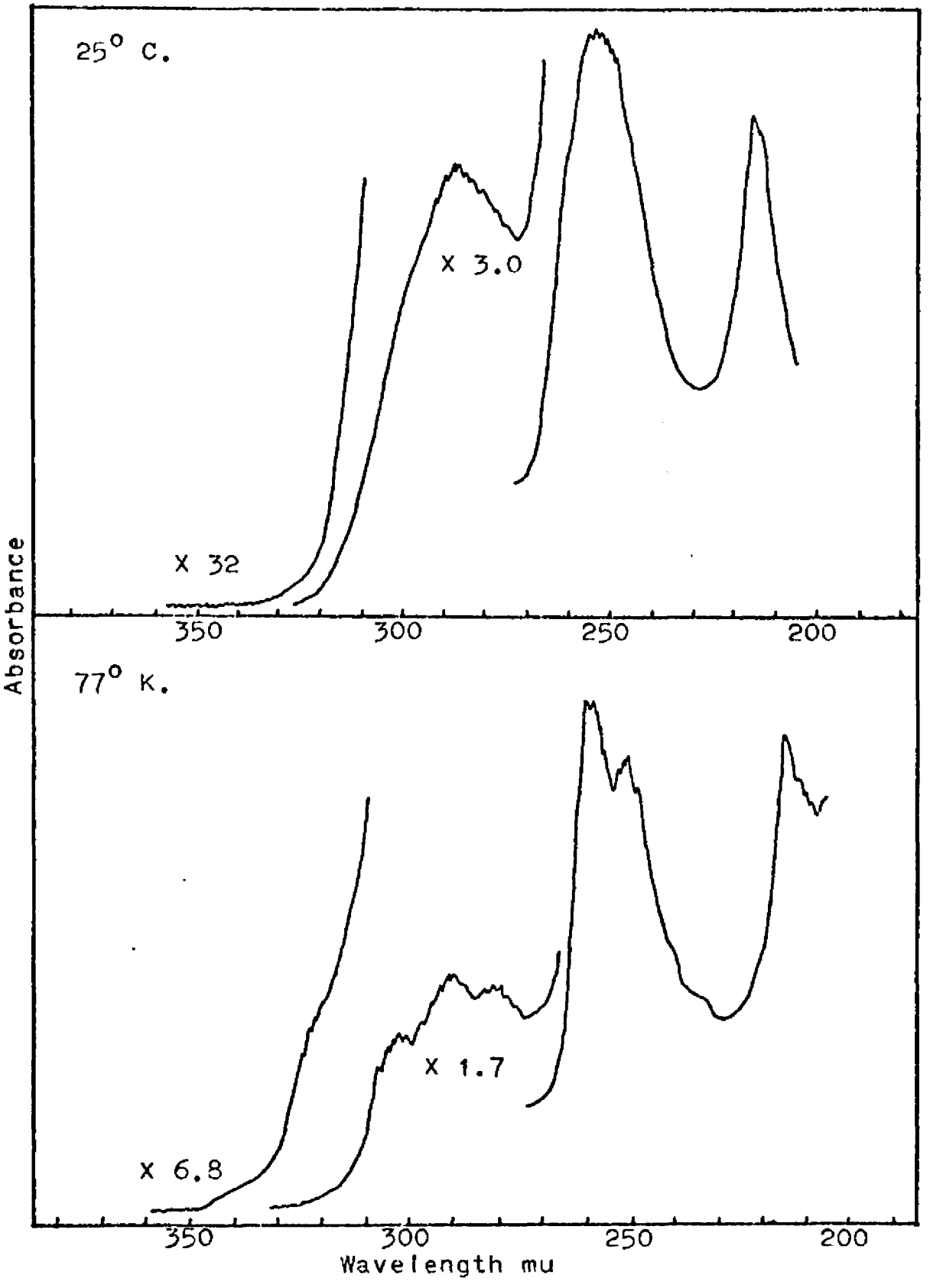


FIGURE 24. Room Temperature and 77° K. Absorption of 4'-chloro-2-phenylnaphthalene in Hydrocarbon

TABLE XVIII

Absorption Frequencies and Extinction Coefficient of 4'-Chloro-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
3250	30,769	6.40×10^{2}
2880	34,722	1.46×10^{4}
2550	39,216	5.28×10^{4}
2150	46,512	4.24×10^{4}

77°K in 3-MPIP

A	Cm.$^{-1}$	$\Delta \nu$
3420	29,240	0
3300	30,303	1063
3190	31,348	2108
3020	33,113	0
2910	34,364	1251
2805	35,651	2538
2710	36,900	3787
2595	38,536	0
2520	39,683	1147
2150	46,512	0

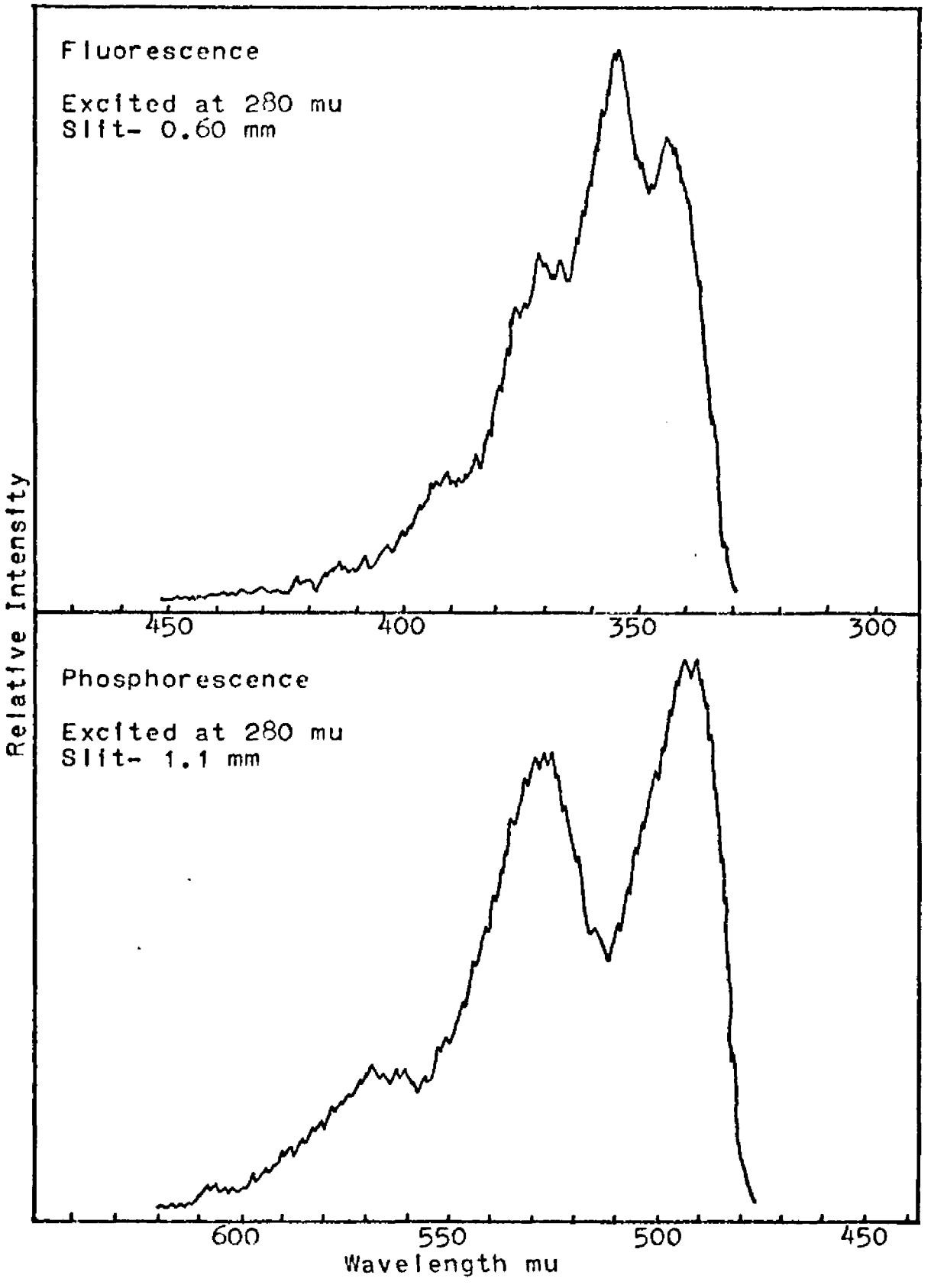


FIGURE 25. 77° K. Fluorescence and Phosphorescence pf 4'-chloro-2-phenylnaphthalene in 3-methylpentane

TABLE XIX

Emission Frequencies of 4'-Chloro-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3420	29,240	0
3570	28,011	1229
3730	26,810	2430
3905	25,608	3632

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
4930	20,284	0
5275	18,957	1327
5670	17,637	2647

in which the molecules are planar. Judging from the observed temperature shifts of the more intense bands, the 0,0 band for the predominate configuration of the molecule in solution should be near 30,400 $cm.^{-1}$. Thus the predomonant configuration at low temperature is interpreted to be non-planar as was that of 2-phenylnaphthalene.

The 0,0 band of the fluorescence emission is observed at 29,240 $cm.^{-1}$ and corresponds to the 0,0 band attributed to the crystal. The indication is, therefore, that the equilibrium excited state molecule has a planar configuration.

The room temperature and 77°K absorption spectra of 4'-bromo-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 26 and the corresponding spectral data are given in Table XX. The fluorescence and phosphorescence emission spectra measured in 3-MP at 77°K are shown in Figure 27 and the emission frequencies are given in Table XXI.

The absorption spectrum of 4'-bromo-2-phenylnaphthalene is similar to that of 4'-chloro-2-phenylnaphthalene. The $^1L_a \leftarrow {}^1A$, $^1B_b \leftarrow {}^1A$ and $^1C_b \leftarrow {}^1A$ transitions are red-shifted 110 $cm.^{-1}$, 150 $cm.^{-1}$ and 0 $cm.^{-1}$ respectively from those of 4'-chloro-2-phenylnaphthalene. If the $^1L_b \leftarrow {}^1A$ transition of 4'-chloro-2-phenylnaphthalene had been interpreted to be at 29,240 $cm.^{-1}$, then the $^1L_b \leftarrow {}^1A$ transition of the 4'-bromo-2-phenylnaphthalene would be blue-shifted 340 $cm.^{-1}$ from this transition. This is inconsistent with the predominant red-shifts observed for the other transitions and is further evidence that the longest wavelength absorption observed in the case of the 4'-chloro derivative is due to a small concentration of crystals.

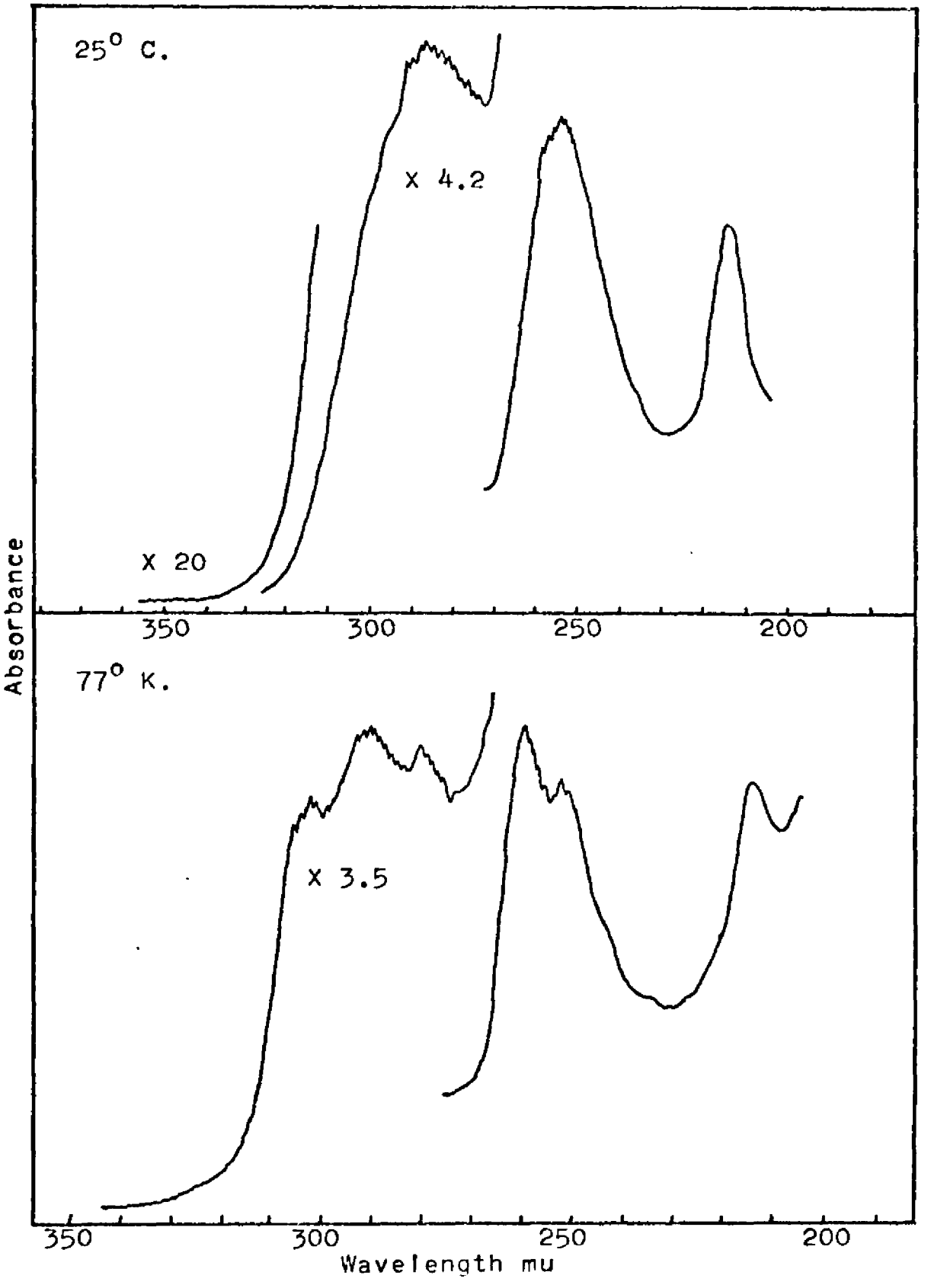


FIGURE 26. Room Temperature and 77° K. Absorption of 4'-bromo-2-phenylnaphthalene in Hydrocarbon

TABLE XX

Absorption Frequencies and Extinction Coefficients of 4'-Bromo-2-Phenylnaphthalene

25°C in 3-MP

A	$Cm.^{-1}$	ϵ(liter/mole cm.)
3230	30,960	7.20×10^2
2880	34,722	1.49×10^4
2550	39,216	5.12×10^4
2150	46,512	3.92×10^4

77°K in 3-MP IP

A	$Cm.^{-1}$	$\Delta \nu$
3380	29,586	0
3260	30,675	1089
3030	33,003	0
2915	34,305	1302
2805	35,651	2648
2705	36,969	3966
2605	38,388	0
2530	39,526	1138
2150	46,512	0

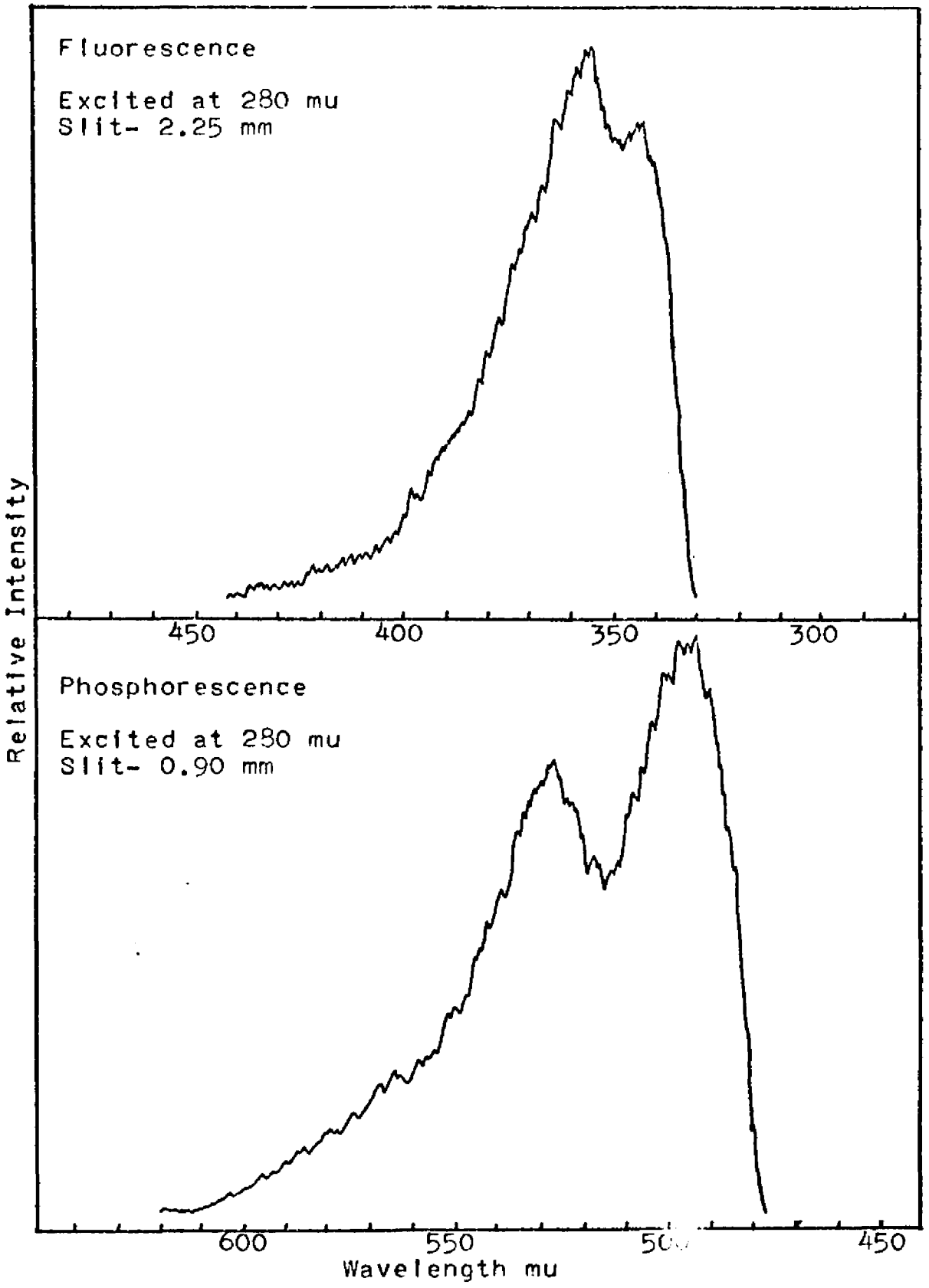


FIGURE 27. 77° K. Fluorescence and Phosphorescence of 4'-bromo-2-phenylnaphthalene in 3-methylpentane

TABLE XXI

Emission Frequencies of 4'-Bromo-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta\nu$
3430	29,155	0
3560	28,090	1065
3700	27,027	2128
3850	25,974	3181

Phosphorescence

A	Cm.$^{-1}$	$\Delta\nu$
4950	20,202	0
5280	18,939	1263
5660	17,668	2534

The 0,0 band of the fluorescence of 4'-bromo-2-phenylnaphthalene is slightly red-shifted (90 cm.$^{-1}$) from that of 4'-chloro-2-phenylnaphthalene. This observation is consistent with an interpretation that the equilibrium excited state of 4'-bromo-2-phenylnaphthalene has a planar configuration. The observation that the 0,0 band of fluorescence is red-shifted only 430 cm.$^{-1}$ from the 0,0 band of absorption indicates that the difference in planarity between the equilibrium ground state and equilibrium excited state is not as great in the case of 4'-bromo-2-phenylnaphthalene as it is in that of 2-phenylnaphthalene. This observation indicates that halogen substitution in the 4'-position may increase the resonance interaction between the two aromatic rings. The slightly higher vibrational frequency of the excited state (1090 cm.$^{-1}$) compared to that of the ground state (1060 cm.$^{-1}$) is an indication that some differences in geometry do exist between the two states.

F. Spectra of 6-Bromo-2-Phenylnaphthalene

The study of 6-bromo-2-phenylnaphthalene was carried out primarily to determine the spin-orbital coupling effect of bromine in the 6-position. The spectra are presented for comparison with those of the other 2-phenylnaphthalene derivatives.

The room temperature and 77°K absorption spectra of 6-bromo-2-phenylnaphthalene in 3-MP and 3-MPIP respectively are shown in Figure 28 and the corresponding spectral data are given in Table XXII. The fluorescence and phosphorescence spectra of the compound in 3-MP at

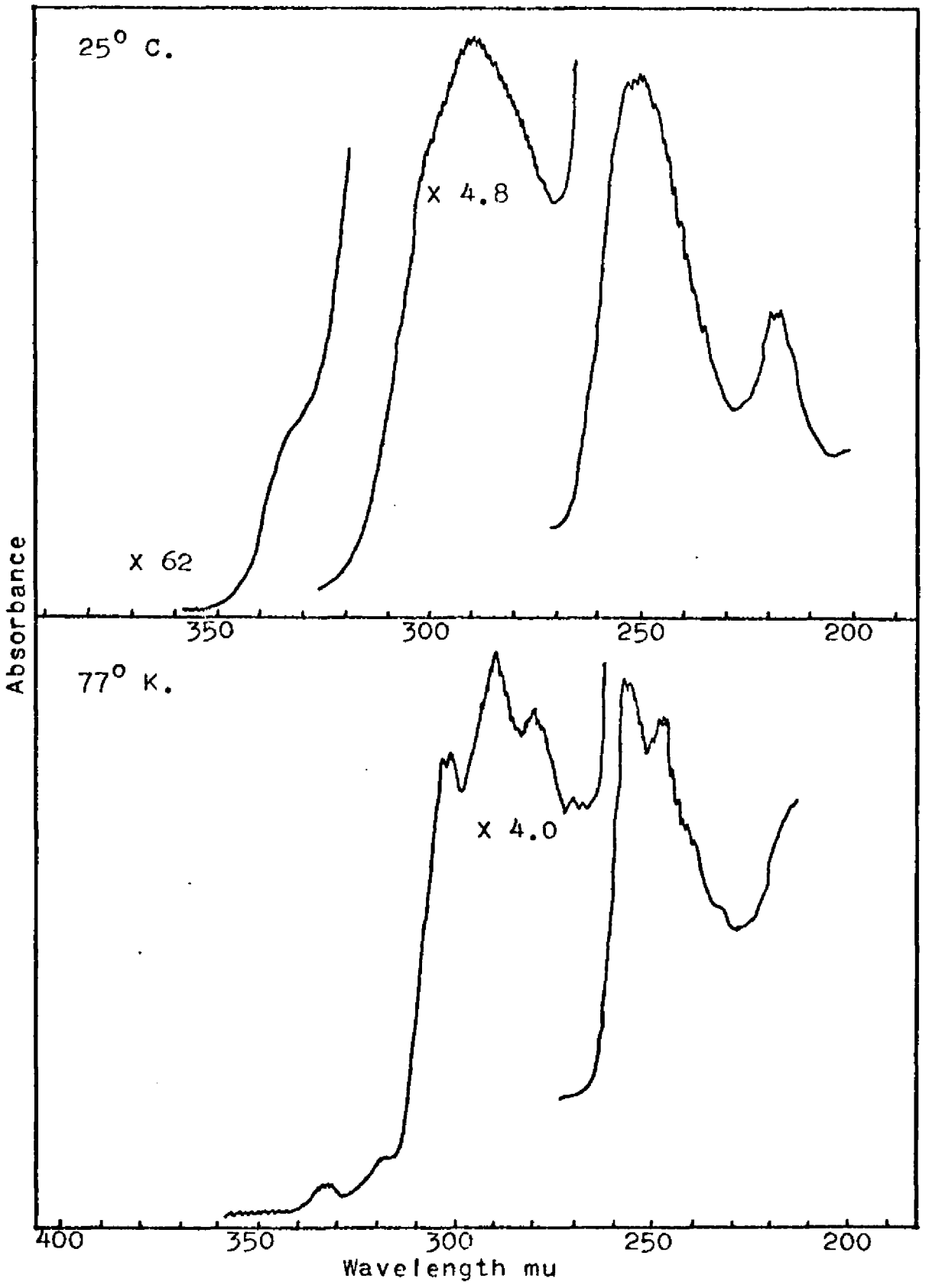


FIGURE 28. Room Temperature and 77° K. Absorption of 6-bromo-2-phenylnaphthalene in Hydrocarbon

TABLE XXII

Absorption Frequencies and Extinction Coefficients
of 6-Bromo-2-Phenylnaphthalene

25°C in 3-MP

A	Cm.$^{-1}$	ϵ(liter/mole cm.)
3320	30,120	4.50×10^{2}
2900	34,483	1.47×10^{4}
2520	39,683	6.10×10^{4}
2180	45,872	3.47×10^{4}

77°K in 3-MPIP

A	Cm.$^{-1}$	$\Delta \nu$
3335	29,985	0
3195	31,299	1314
3040	32,895	0
2925	34,188	1293
2820	35,461	2566
2720	36,765	3870
2575	38,835	0
2500	40,000	1165
2130	46,948	0

77°K are shown in Figure 29 and the corresponding emission frequencies are given in Table XXIII.

The 77°K absorption spectrum of 6-bromo-2-phenylnaphthalene is very much like that of 2-phenylnaphthalene except for some red-shifts due to extension of conjugation by the bromine atom. The $^1L_b \leftarrow {}^1A$, $^1L_a \leftarrow {}^1A$ and $^1B_b \leftarrow {}^1A$ transitions are red-shifted 1020 cm.$^{-1}$, 320 cm.$^{-1}$ and 380 cm.$^{-1}$ respectively compared with those of 2-phenylnaphthalenes. There is no evidence for a 90 degree configuration in 6-bromo-2-phenylnaphthalene.

The 0,0 band of the fluorescence spectrum at 29,370 cm.$^{-1}$ is red-shifted 620 cm.$^{-1}$ from the 0,0 band of absorption at 29,990 cm.$^{-1}$. This indicates an appreciable difference in the planarity of the equilibrium ground state and the equilibrium excited state of 6-bromo-2-phenylnaphthalene. Since the fluorescence frequencies are in approximately the region expected for emission from a planar excited state and the Franck-Condon band contour resembles that of 2-phenylnaphthalene, it is concluded that, like 2-phenylnaphthalene, 6-bromo-2-phenylnaphthalene has a non-planar equilibrium ground state and a planar equilibrium excited state. Due to the smaller difference between 0,0 bands of fluorescence and absorption (620 cm.$^{-1}$) compared with that of 2-phenylnaphthalene (1770 cm.$^{-1}$), it may be concluded that 6-bromo-2-phenylnaphthalenes has a slightly smaller angle in the equilibrium ground state than does 2-phenylnaphthalenes.

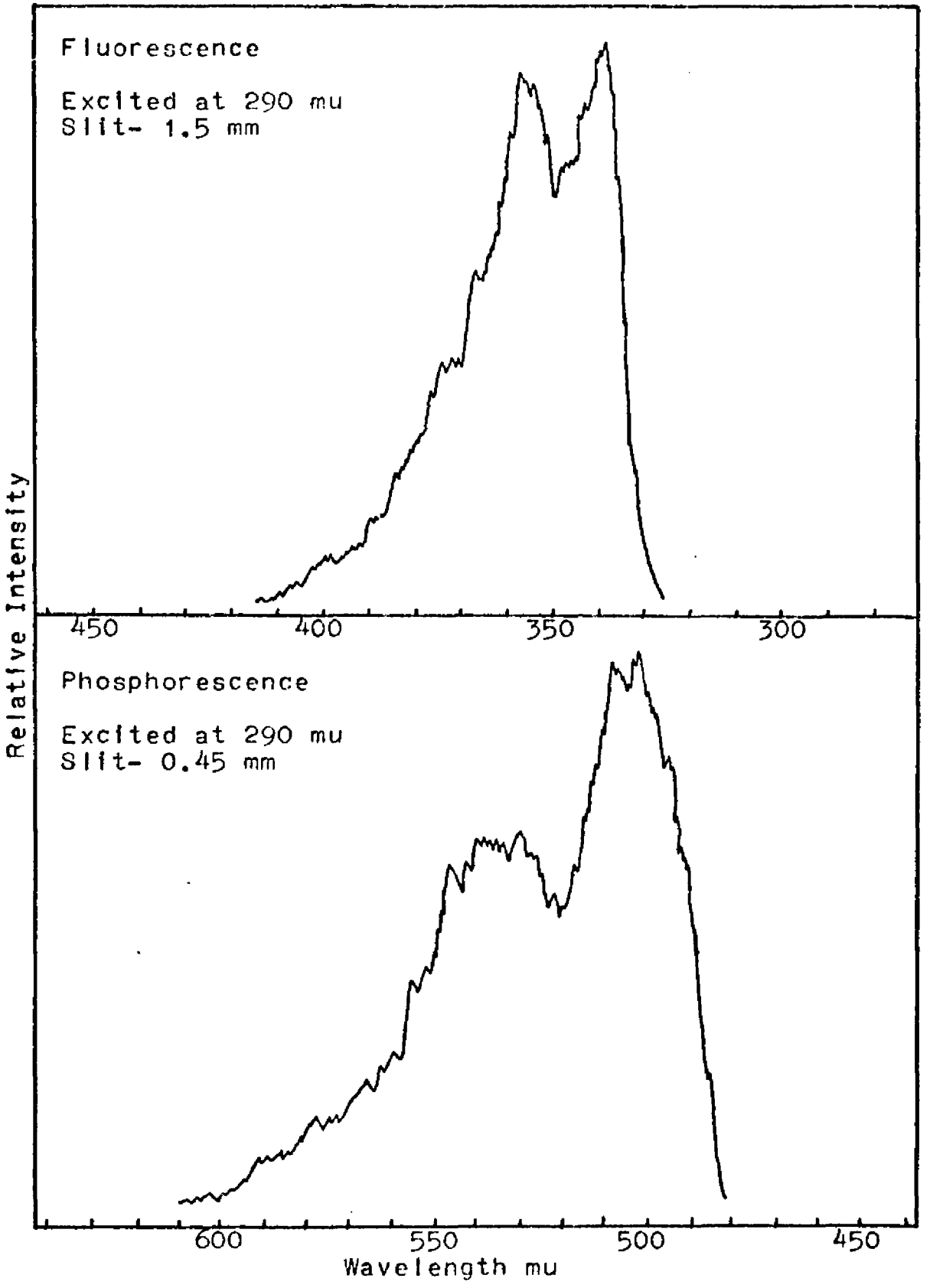


FIGURE 29. 77° K. Fluorescence and Phosphorescence of 6-bromo-2-phenylnaphthalene in 3-methylpentane

TABLE XXIII

Emission Frequencies of 6-Bromo-2-Phenylnaphthalene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3405	29,369	0
3480	28,735	634
3560	28,090	1279
3640	27,473	1896
3725	26,846	2523
3815	26,212	3157
3910	25,575	3794

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
5035	19,861	0
5380	18,587	1274
5780	17,301	2560

G. Spectra of 1,2-Benzfluorene

If the ideas presented in section D on the 1-halo-2-phenylnaphthalenes have any validity, there should be similarities between the spectral frequencies of these compounds and 1,2-benzfluorene. 1,2-benzfluorene may be considered to be a 2-phenylnaphthalene held rigidly in plane by a methylene bridge. 1,2-benzfluorene would be expected to have the more extensive vibrational structure, that has been generally observed by Jones[64] in the case of compounds of this type.

The room temperature and 77°K absorption spectra of 1,2-benzfluorene in 3-MP and 3-MPIP respectively are shown in Figure 30 and the 77°K absorption frequencies are given in Table XXIV. The fluorescence and phosphorescence spectra of 1,2-benzfluorene in 3-MP at 77°K are shown in Figure 31 and the corresponding emission frequencies are given in Table XXV.

In all probability the first absorption band at 29,110 $cm.^{-1}$ in the 77°K absorption spectrum of 1,2-benzfluorene is not the 0,0 band. There is a perfect match of the frequency of the second absorption band at 29,450 $cm.^{-1}$ with that of the 0,0 band of fluorescence. Since the intensity of the first absorption band decreased with decreasing temperature, it is concluded that the first band may be a hot band and that the second band in the absorption spectrum is the 0,0 band. More extensive temperature

---

[64] R. N. Jones, J. Am. Chem. Soc., 67, 1945, p. 2131.

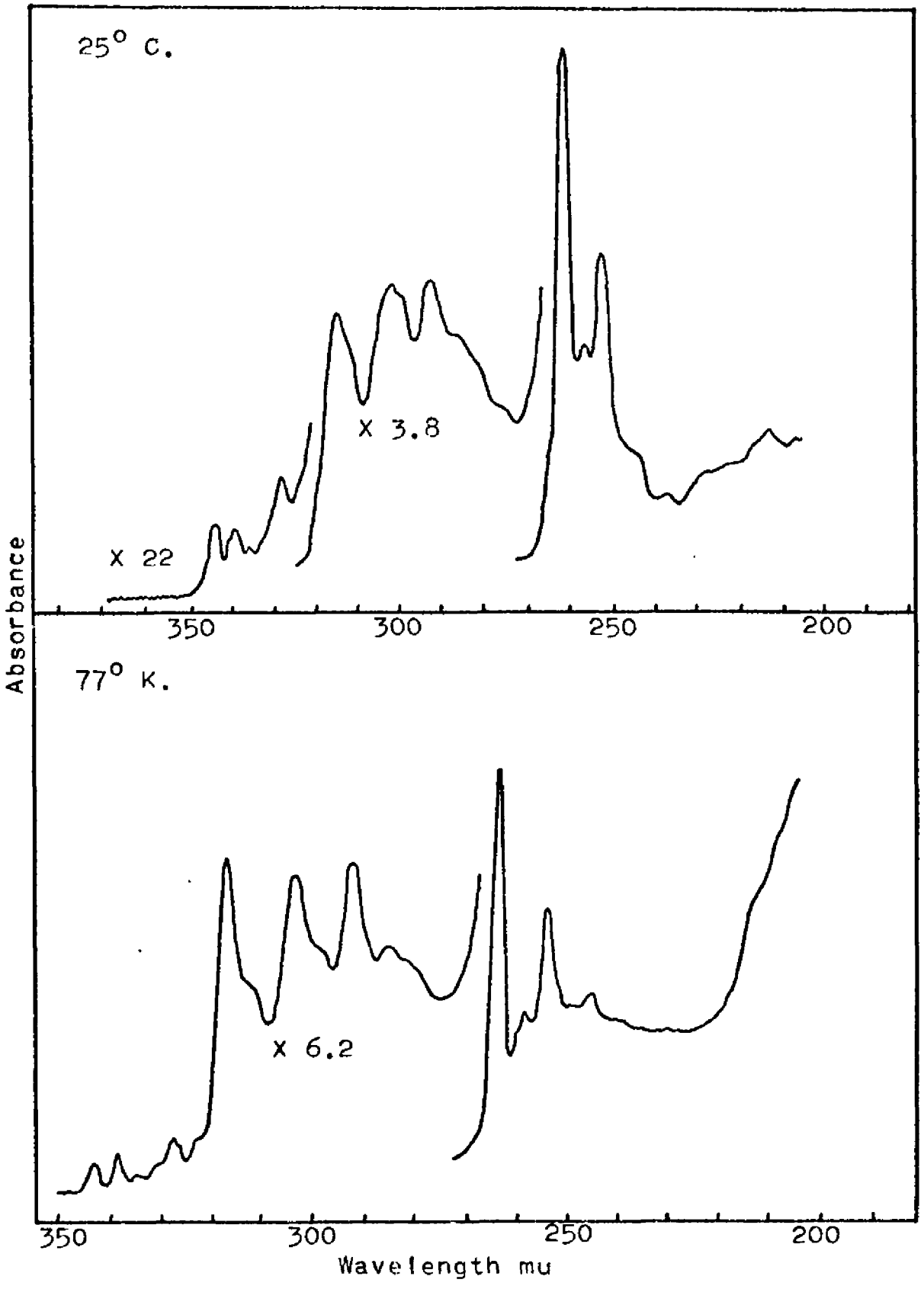


FIGURE 30. Room Temperature and 77° K. Absorption of 1,2-benzfluorene in Hydrocarbon

TABLE XXIV

77° K Absorption Frequencies of 1,2-Benzfluorene

A	Cm.$^{-1}$	$\Delta \nu$
3435	29,112	0
3395	29,455	343
3355	29,806	694
3315	30,166	1054
3275	30,534	1422
3235	30,912	1800
3185	31,397	0
3115	32,103	706
3050	32,787	1390
2985	33,501	2104
2930	34,130	2733
2870	34,843	3446
2635	37,951	0
2590	38,610	659
2545	39,293	1342
2500	40,000	2049
2460	40,650	2699

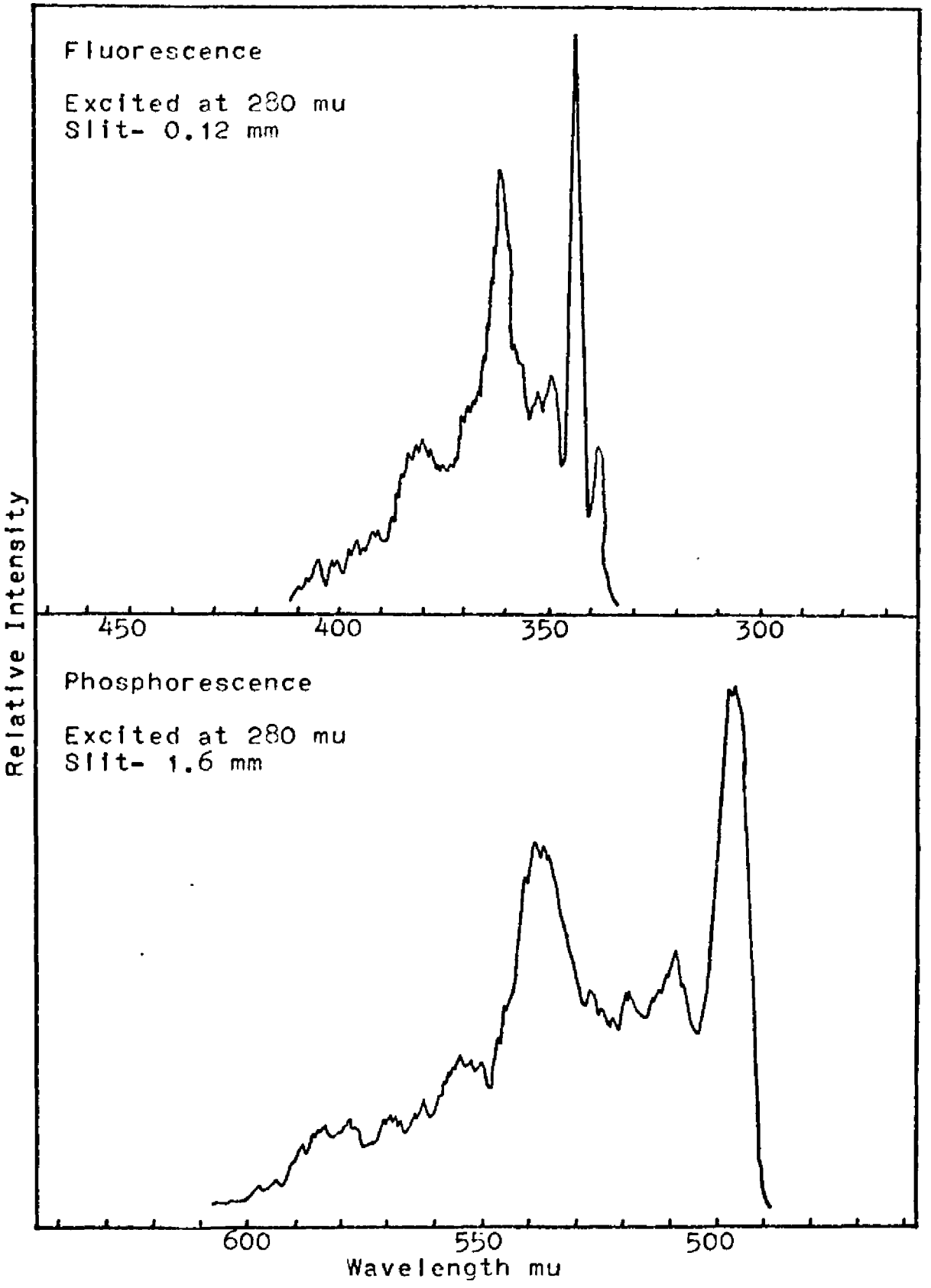


FIGURE 31. 77° K. Fluorescence and Phosphorescence of 1,2-benzfluorene in 3-methylpentane

TABLE XXV

Emission Frequencies of 1,2-Benzfluorene

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
3395	29,455	0
3440	29,070	385
3505	28,531	924
3530	28,329	1126
3575	27,972	1483
3620	27,624	1831
3720	26,882	2573
3820	26,178	3277
4050	24,691	4764

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
4980	20,080	0
5095	19,627	453
5195	19,249	831
5270	18,975	1105
5380	18,587	1493
5550	18,018	2062
5830	17,153	2927

studies need to be performed to definitely assign the first band as a hot band. There is a good mirror image relationship between absorption and fluorescence of 1,2-benzfluorene. It is indicated, therefore, that the ground state and excited state geometries are similar. It is assumed that both states correspond to a planar configuration.

There is a great deal of similarity between the absorption and emission frequencies of 1,2-benzfluorene and those of the 1-halo-2-phenylnaphthalenes. Except for the additional vibrational structure in the 1,2-benzfluorene spectra, the general appearance of all the spectra are similar. The frequencies of the 0,0 bands of absorption and emission of 1,2-benzfluorene and the 1-halo-2-phenylnaphthalenes are given in Table XXVI for comparison.

TABLE XXVI

Comparison of 0,0-Bands of 1,2-Benzfluorene and 1-Halo-2-Phenylnaphthalenes

Compound	Absorption 0,0 Band (A)	Fluorescence 0,0 Band (A)
1,2-benzfluorene	3395	3395
1-fluoro-2-phenylnaphthalene	3280	3320
1-chloro-2-phenylnaphthalene	3360	3400
1-bromo-2-phenylnaphthalene	3370	-

The frequencies of all the 0,0 bands are very close to one another. Some variations must be expected because of inductive effects of halogen substitution. There is also the possibility of increased resonance interaction through the methylene linkage of 1,2-benzfluorene compared with that of the 1-halo-2-phenylnaphthalenes. This comparison is not conclusive evidence that the 1-halo-2-phenylnaphthalenes are planar in the equilibrium ground state, however, it does indicate that the amount of red-shift observed in the 1-halo-2-phenylnaphthalenes is consistent with an amount to be expected if the experimental evidence is interpreted to indicate that there is a planar or near-planar ground state configuration.

H. Spin-Orbital Coupling and the Triplet State of 2-Phenylnaphthalene Derivatives

The previous discussions concerning geometries of the ground and excited states have given no insight at all into the planarity of the molecules in the triplet state. The same arguments presented for the singlet state cannot be used for the triplet state without first measuring good singlet-triplet absorption spectra. Singlet-triplet absorption spectra are very difficult to obtain because of the forbidden nature of the singlet-triplet transitions. Because of this difficulty a different approach is employed. This approach involves the comparison of spin-orbital coupling effects from halogen substitution at different positions on the 2-phenylnaphthalene molecule.

The phosphorescence spectra of all the compounds studied were measured in rigid glassy 3-MP at 77° K. These spectra are shown with the corresponding fluorescence spectra for convenience. Table XXVII gives the lowest triplet state energy levels and the vibrational frequencies observed in the phosphorescence spectra. The frequencies of the 2-halonaphthalenes are included for comparison.

There is observed very little variation in the lowest triplet state energy levels for the compounds listed in Table XXVII. The lowest triplet level of 2'-methyl-2-phenylnaphthalene (20,900 $cm.^{-1}$) is blue shifted 360 $cm.^{-1}$ from that of 2-phenylnaphthalene (20,530 $cm.^{-1}$). The blue-shift is interpreted to be the result of different triplet state geometries of the two compounds. 2'-methyl-2-phenylnaphthalene would be expected to be non-planar in the triplet state, as was found for the excited singlet state. At least there is no evidence to indicate that it is planar in the triplet state. The triplet levels of 4'-chloro-2-phenylnaphthalene, 4'-bromo-2-phenylnaphthalene and 6-bromo-2-phenylnaphthalene are all somewhat lower than those of the other compounds. This can be attributed to extension of conjugation by halogen substitution.

The normal trend of decreasing vibrational frequency with increasing mass of a substituent is observed in the 1-halo-2-phenylnaphthalene series. The same decreasing trend is observed in the results from the fluoro and chloro 2'-halo derivatives, but there is an abrupt increase in emission frequency and in vibrational frequency in the case of 2'-bromo-2-phenylnaphthalene. This discontinuity in

TABLE XXVII

Lowest Triplet State Energy Levels and Vibrational Frequencies of Naphthalene Derivatives

Compound	Frequency of 0,0 Band ($Cm.^{-1}$)	Vibrational Frequency ($Cm.^{-1}$)
naphthalene	21,299	1420
2-fluoronaphthalene	21,322	1380
2-chloronaphthalene	21,097	1370
2-bromonaphthalene	21,097	1370
2-phenylnaphthalene	20,534	1410
2'-methyl-2-phenylnaphthalene	20,899	1425
1-fluoro-2-phenylnaphthalene	20,576	1450
1-chloro-2-phenylnaphthalene	20,367	1425
1-bromo-2-phenylnaphthalene	20,408	1400
2'-fluoro-2-phenylnaphthalene	20,661	1430
2'-chloro-2-phenylnaphthalene	20,408	1380
2'-bromo-2-phenylnaphthalene	20,555	1410
4'-chloro-2-phenylnaphthalene	20,284	1330
4'-bromo-2-phenylnaphthalene	20,202	1270
6-bromo-2-phenylnaphthalene	19,861	1280
1,2-benzfluorene	20,080	1440

this series probably results from a radical change in geometry of the triplet state molecule.

The phosphorescence lifetime of a molecule is a reciprocal of the total radiative and non-radiative transition probability from the lowest excited triplet state to the ground state. The magnitude of this transition probability is one measure of the spin-orbital coupling effects in the molecule. In order for a heavy atom substituent to have the same spin-orbital coupling effect at different positions on a molecule, the electrons influenced by the heavy atom must spend the same amount of time at the different positions. If the naphthalene subsystem is the chromophore in 2-phenylnaphthalene then heavy-atom substitutions in the phenyl ring should have little effect on spin orbital coupling except in cases in which external heavy atom effects or vibrational perturbations are possible. If the entire molecule is considered to be the chromophore then heavy-atom substitution on the two rings should give some indication of the relative electron densities in the two rings. Normally the electronic densities of the 2' and 4' positions of 2-phenylnaphthalene would be expected to be identical, therefore, differences in spin-orbital coupling effects between these two positions would be a measure of the difference in co-planarity of the aromatic rings when they are substituted in these two different positions. Phosphorescence lifetimes then are not only dependent on the heavy-atom substituent but also on the position of the substituent and the geometry of the molecule.

Dependence of the extent of intersystem crossing is not as simple as that of phosphorescence lifetimes. Intersystem crossing also depends on spin-orbital coupling and hence is affected by the halogen substituent, position of the substituent and geometry of the triplet state; in addition it depends on the lifetime of the lowest excited singlet state, and the geometric configuration of the molecule in the excited singlet state. The ratio of phosphorescence to fluorescence quantum yields can be used as an indication of the extent of intersystem crossing but, because of the many variables that control intersystem crossing, it is difficult to draw definite conclusions about the exact origin of observed changes in quantum yield ratios.

Phosphorescence lifetimes and quantum yields for both fluorescence and phosphorescence were measured for all the 2-phenylnaphthalene derivatives. The phosphorescence lifetimes are given in Table XXVIII and the quantum yields are given in Table XXIX.

It is observed in the lifetime data given in Table XXVIII that the phenyl ring in 2'-methyl-2-phenylnaphthalene has a small spin-orbital coupling effect compared to that of naphthalene. The effect is even greater in 2-phenylnaphthalene, indicating that there is probably some difference in the configurations of the two molecules in the triplet state. It can only be presumed that the difference in spin orbital coupling reflects a difference in planarity between the two systems. The value of Φ_P/Φ_F for 2'-methyl-2-phenylnaphthalene (.072) is higher than for 2-phenylnaphthalene (.056). This is difficult to rationalize on the basis of spin-orbital coupling alone.

TABLE XXVIII

Phosphorescence Lifetimes of 2-Phenylnaphthalene Derivatives

Compound	Lifetime (sec.)	$1/\tau_p = K_P + K_{QP}$ (sec.$^{-1}$)
naphthalene	2.5	0.40
2-phenylnaphthalene	1.8	0.56
1-fluoro-2-phenylnaphthalene	1.8	0.56
1-chloro-2-phenylnaphthalene	0.29	3.4
1-bromo-2-phenylnaphthalene	0.048	21
6-bromo-2-phenylnaphthalene	0.52	1.9
2'-methyl-2-phenylnaphthalene	2.1	0.48
1,2-benzfluorene	2.8	0.36
2'-fluoro-2-phenylnaphthalene	2.6	0.38
2'-chloro-2-phenylnaphthalene	2.3	0.43
2'-bromo-2-phenylnaphthalene	0.28	3.6
4'-chloro-2-phenylnaphthalene	1.7	0.59
4'-bromo-2-phenylnaphthalene	0.19	5.3

TABLE XXIX

Phosphorescence and Fluorescence Quantum Yields
for 2-Phenylnaphthalene Derivatives

Compound	Φ_F	Φ_P	Φ_P/Φ_F
naphthalene	0.45	0.011	0.024
2-phenylnaphthalene	0.34	0.019	0.056
1-fluoro-2-phenylnaphthalene	0.39	0.020	0.051
1-chloro-2-phenylnaphthalene	0.051	0.049	0.96
1-bromo-2-phenylnaphthalene	~0.0013	0.17	~130
6-bromo-2-phenylnaphthalene	~0.0058	0.066	~ 11
1,2-benzfluorene	0.995	0.0045	0.0045
2'-methyl-2-phenylnaphthalene	0.25	0.018	0.072
2'-fluoro-2-phenylnaphthalene	0.29	0.025	0.086
2'-chloro-2-phenylnaphthalene	0.28	0.027	0.096
2'-bromo-2-phenylnaphthalene	~0.00055	0.25	~450
4'-chloro-2-phenylnaphthalene	0.19	0.059	0.31
4'-bromo-2-phenylnaphthalene	~0.017	0.11	~6.5

The increase, it can be seen, is not due to an increase in Φ_P but to a decrease in Φ_F. This is probably due to a change in fluorescence lifetime of 2'-methyl-2-phenylnaphthalene compared with that of 2-phenylnaphthalene. The value of Φ_P/Φ_F in this case gives little information concerning the planarity of the triplet state of 2'-methyl-2-phenylnaphthalene.

The trends observed in the 1-halo-2-phenylnaphthalenes are essentially those that were expected. There is the normal increase in Φ_P/Φ_F as the lifetimes decrease with increasing atomic number of the heavy-atom substituent. The heavy-atom effects observed in the phosphorescence of the 2'-halo and 4'-halo derivatives are less than those observed when the same substituents are in the 1-position. The lifetimes of the 2'-halo-2-phenylnaphthalenes are substantially longer in all cases than those for the corresponding 1-halo derivatives; those of the 4'-halo-2-phenylnaphthalenes are longer than for the 1-halo derivatives but are shorter than those of the corresponding 2'-halo derivatives. The decrease in spin-orbital coupling with halogen substitution in the phenyl ring compared to that in the case of substitution in the naphthalene ring must be due to geometry changes that tend to cancel some of the effect observed with 1-halo substitution. One interpretation of this difference is that the phenyl ring is slightly out of plane when there is 2' and 4'-substitutions and more nearly planar in the case of 1-halo substitution, hence there is less interaction of the two rings in the triplet state when there is 2'- and 4'-substitution. The fact that the spin-orbital

coupling effect is greater in the 4'-position than in the 2'-position is good evidence that there is a difference in the geometries of the two systems, since normally the electronic densities of these two positions on the phenyl ring are the same. On the basis of lifetime data alone the indication is that the 2'-halo-2-phenylnaphthalenes are more out of plane in the triplet state than are the corresponding 4'-halo derivatives.

The phosphorescence lifetime of 6-bromo-2-phenylnaphthalne (0.52 sec.) is substantially longer than that of 1-bromo-2-phenylnaphthalene (0.048 sec.). This indicates that there must be a much lower electronic density at the 6-position than at the 1-position of the 2-phenylnaphthalene molecule in the triplet state.

The effect of heavy-atom substituents on the extent of intersystem crossing in many of these compounds is not as straignt forward as is the effect on phosphorescence lifetimes. From the data in Table XXIX it is observed that the increase in Φ_p/Φ_f with increase in atomic number of the halogen substituents is apparently rather normal in the case of the 1-halo-2-phenylnaphthalenes except in that of 1-fluoro-2-phenylnaphthalene, in which Φ_p/Φ_f decreases from the value for 2-phenylnaphthalene. This is apparently due to an increase in fluorescence yield rather than a decrease in phosphorescence. This phenomenon has been observed before in fluoro-derivatives and has been attributed to decreased vibrational overlap by Bhaumik and Nugent.[65]

---

[65] M. Bhaumik and L. Nugent, J. Chem. Phys., 43, 1965, p. 1680.

As in the case of the phosphorescence lifetimes the values of Φ_P/Φ_F for the 2'-fluoro and 2'-chloro-2-phenylnaphthalene seem to change in the expected direction with heavy atom substitution but the magnitude of the change is reduced from that expected from comparison with the results from 1-halo derivatives. The value of Φ_P/Φ_F for 2'-bromo-2-phenylnaphthalene (450) increases by an abnormally large amount, a factor of 4,500 over that of 2'-chloro-2-phenylnaphthalene. Φ_P/Φ_F for 1-bromo-2-phenylnaphthalene only increases by a factor of 130 over that of 1-chloro-2-phenylnaphthalene. Since 2'-bromo substitution has a much larger spin-orbital coupling effect on intersystem crossing than it does on phosphorescence lifetime, there is an indication that the abnormally large effect is due to geometry differences in the excited singlet state from which the intersystem crossing occurs. Absorption data has shown that there is a relatively large population of 90 degree configuration molecules in the ground state and possibly there is also a large population in the excited state of 2'-bromo-2-phenylnaphthalene. Molecules of this compound that were 90 degrees out of plane would have the 2'-bromine atom in close proximity to the pi cloud of the naphthalene subsystem, hence there should be a very efficient external heavy-atom effect from the bromine atom. This effect would not be as great in the case of the 2'-chloro derivative because the 90 degree population in this case is small and the small size of the chlorine atom would prevent it from approaching as closely to the naphthalene pi cloud. Because the extremely large spin-orbital

coupling effect does not appear in the phosphorescence lifetimes, it can be assumed that the 2'-bromo-2-phenylnaphthalene does not have a 90 degree configuration in the lowest excited triplet state.

Comparison of the Φ_p/Φ_f results from the 4'-halo-2-phenylnaphthalenes with those of the 1-halo-2-phenylnaphthalenes shows that the spin orbital coupling effect is decreased when there is substitution in the 4'-position; the lifetime data supported a similar conclusion.

On the basis of lifetime data alone one could rank the spin-orbital coupling effect of bromine substitution at various positions on the 2-phenylnaphthalene molecule in the order 1 > 4' > 2' > 6. The same order would not be obtained by using the Φ_p/Φ_f data; changes in geometry of the excited singlet states may cause the difference. The chloro compounds may be ranked on the basis of Φ_p/Φ_f or phosphorescence lifetimes in the order 1 > 4' > 2'.

On the basis of the available experimental data it is possible to make some generalizations concerning the nature of the chromophore in 2-phenylnaphthalene. The spin orbital coupling effects observed in the 1, 6 and 4'-halo substituted 2-phenylnaphthalenes indicate that the phenyl ring is part of the triplet state chromophore from which phosphorescence emission is observed. One might tend to explain the heavy-atom effect in the 4'-halo derivatives as being due to a spin-orbital coupling effect on a naphthalene chromophore at a distance or to vibrational perturbations by the halogen. Both these explanations appear unlikely. A heavy-atom spin-orbital coupling

affect, as exhibited by changes in phosphorescence lifetimes, varies as $1/r^6$,[66] in which r is the distance from the excited electron to the nucleus of the heavy atom. On this basis the effect in the 4'-position would be very small compared with that in the 6-position, if one assumes the chromophore to be naphthalene. This does not agree with the experimental observations. Vibronic perturbations due to halogen substitution may cause changes in the phosphorescence lifetimes, however, such perturbations usually tend to increase the phosphorescence lifetime. This has been observed many times in cases in which deuterium atoms were substituted for hydrogen atoms. The relative change in phosphorescence lifetimes between chlorine and bromine substitution for the 4'-position is about the same as that observed in the case of the 1-position substitutions. Since in all probability there is a normal heavy-atom spin-orbital coupling effect in the case of the 1-halo-2-phenylnaphthalenes even for a naphthalene chromophore, one would tend to believe that a similar effect is also operative in the 4'-position. In the opinion of the writer, if the naphthalene subsystem were the emitting species, then there should be essentially no heavy-atom effect due to halogen substitution in the 4'-position. The same statement cannot be made about the 2'-position because of possible external heavy-atom effects in this position. The data indicate that halogen substitution in the 4'-position is more effective in promoting spin-orbital coupling than

---

[66] S. K. Lower and M. A. El-Sayed, loc. cit.

is that in the 6-position on the naphthalene ring. The phenyl ring, therefore, must be rather strongly involved as part of the triplet state chromophore.

If one could obtain a 2-phenylnaphthalene molecule with the aromatic rings held firmly at the 90 degree configuration, it might be possible to still speak of an independent naphthalene subsystem in the excited state, however, the data have clearly shown that the more planar excited states are more stable, hence the independent naphthalene subsystem excited state is a very unlikely situation.

From the observed vibrational frequencies in the phosphorescence spectra, there is some indication that the ground state of 2-phenylnaphthalene may be vibronically similar to that of naphthalene. This may indicate that the excited electron spends relatively more time in the naphthalene portion of the molecule than in the benzene portion.

I. Comparisons of Experimental and Calculated Spectral Data for Planar 2-Phenylnaphthalene

A semiempirical Self Consistent Field Molecular Orbital (SCFMO) calculation by the method formulated by Pariser, Parr and Pople was carried out on planar 2-phenylnaphthalene, the geometric configuration of which is shown in Figure 10. The Pariser, Parr and Pople method is described in Chapter I.

The energy levels, transition moments, and polarizations from the calculations are compared with the experimental energy levels and extinction coefficients in Table XXX. The experimental energy level for the $^1L_b \leftarrow {}^1A$ transition is from the fluorescence emission, since it is believed to be an emission from a planar molecule.

The calculations indicate the existence of an extremely weak transition at 46,700 $cm.^{-1}$. The presence of a band of very low intensity would be difficult to detect, since it is very close to the observed frequency of the $^1C_b \leftarrow {}^1A$ transition (47,170 $cm.^{-1}$). There is observed in the room temperature spectrum of 2-phenylnaphthalene what appears to be a very weak transition at approximately 44,000 $cm.^{-1}$. This may correspond to the calculated transition at 46,700 $cm.^{-1}$. Most of the frequencies and relative intensities are in fair agreement with those observed experimentally.

The charge densities on all the carbon atoms were calculated to be essentially unity for the ground state of planar 2-phenylnaphthalene. The charge densities for the ^1L_b excited state and all bond orders for both the ground state and the ^1L_b excited state were calculated. The bond orders were converted to bond lengths and the results are shown in Table XXXI. The numbering system is based on the following system:

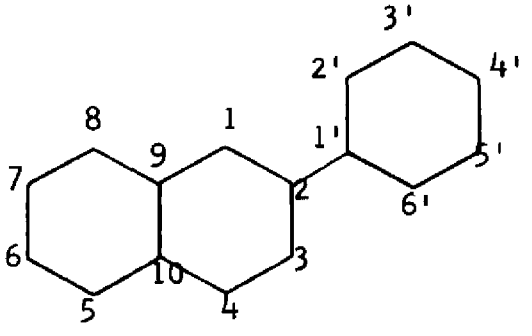


TABLE XXX

Calculated and Experimental Transitions
of Planar 2-Phenylnaphthalene

Transition	Expt. Energy ($Cm.^{-1}$)	Calc. Energy ($Cm.^{-1}$)	ϵ(liter/mole/cm.)	Transition Moment	Polarization
$^1L_b \leftarrow {}^1A$	29,240	33,120	$\sim 10^2$	.0006	30.5°
$^1L_a \leftarrow {}^1A$	34,840	34,980	1.3×10^4	.8130	36.3°
$^1B_b \leftarrow {}^1A$	40,000	40,460	5.7×10^4	2.0217	-26.2°
$^1C_b \leftarrow {}^1A$	47,170	46,990	4.1×10^4	.5986	-36.7°

It is apparent upon examination of the results in Table XXXI that there have been significant changes in both the charge densities and bond lengths when the molecule is excited to the ^1L_b electronic state. That there has been significant interaction between the two aromatic rings is indicated by the decrease in the length of the bond between the rings from 1.48 A. in the ground state to 1.45 A. in the excited state. It was also observed from the total charge density in the two rings that 0.357 electrons are transferred from the naphthalene to the benzene ring on excitation. This observation is in agreement with the writer's contention that resonance interaction energy should be greater for 2-phenylnaphthalene than for biphenyl because in 2-phenylnaphthalene there is the added possibility of charge transfer between the two rings.

The charge densities reported for the ^1L_b state of planar 2-phenylnaphthalene probably will not be the same as those of the ^3L_a state, however, it is observed that the charge density in the 6-carbon position (.930) is much less than that for the 1-carbon position (1.007). This is in agreement with the experimental observations that bromine substituted in the 6-position has a reduced spin-orbital coupling effect compared to that of bromine substituted in the 1-position. It is also observed that bromine in the 4'-position has a greater spin-orbital coupling effect than that in the 6-position. This is also in agreement with an argument based on the calculated charge densities.

Except for minor energy level differences and some variations in band intensities, nothing in the calculations for planar 2-phenylnaphthalene is in major disagreement with the reported experimental observations.

TABLE XXXI

Calculated Charge Densities and Bond Lengths
for Planar 2-Phenylnaphthalene

Carbon Atom	^1L_b Charge Density	Bond	Ground State Length (A)	^1L_b State Length (A)
1	1.007	1-2	1.37	1.40
2	0.951	2-3	1.40	1.42
3	0.960	3-4	1.36	1.39
4	0.981	4-10	1.41	1.41
5	1.007	10-5	1.41	1.42
6	0.930	5-6	1.36	1.38
7	0.936	6-7	1.40	1.40
8	1.002	7-8	1.36	1.39
9	0.935	8-9	1.41	1.41
10	0.935	9-1	1.41	1.41
1'	1.113	9-10	1.41	1.43
2'	1.034	2-1'	1.48	1.45
3'	1.026	1'-2'	1.39	1.41
4'	1.123	2'-3'	1.38	1.37
5'	1.028	3'-4'	1.38	1.39
6'	1.033	4'-5'	1.38	1.40
		5'-6'	1.38	1.37
		6'-1'	1.39	1.41

CHAPTER IV

SUMMARY AND CONCLUSIONS

The dual emissions previously reported for fluoranthene, 2-phenylnaphthalene and 1,2-benzfluorene have been shown to originate from traces of impurities present in the commercially prepared compounds. The impurities in fluoranthene and 2-phenylnaphthalene could not be removed by any of the conventional purification procedures. Pure compounds could be obtained only by synthesis. 1,2-benzfluorene was sufficiently purified by sublimation to exhibit a single fluorescence and a single phosphorescence. No impurity transitions could be detected in the absorption spectrum of fluoranthene. The absorption spectrum of synthetic fluoranthene was identical with that reported for the sample exhibiting dual emissions, however, the synthetic sample emitted only a single fluorescence and a single phosphorescence. The impurity phosphorescence from fluoranthene resembled that of phenanthrene but it was slightly red-shifted.

The impurity in 2-phenylnaphthalene had the same absorption spectrum as that of anthracene but the vibrational structure in the fluorescence spectrum was somewhat different from that of anthracene. The presence of 2-phenylnaphthalene apparently has the effect of intensifying the antisymmetric vibrational bands of anthracene while

decreasing the intensity of the symmetric vibrational bands. This must be due to some type of complexation in which the 2-phenylnaphthalene alters the geometry of the excited state of anthracene.

Even though the second emissions reported for fluoranthene, 2-phenylnaphthalene and 1,2-benzfluorene have been shown to originate from impurities, this does not necessarily mean that complex molecules of this kind, made up of smaller subsystems, cannot under the proper excitation exhibit the emission properties of the individual subsystems. However, evidence based on the experimental observations in this research tends to indicate that the probability of observing emissions from the independent subsystems of 2-phenylnaphthalene is extremely low.

The uncertainty principle shows that the average time during which one molecule in a crystal may be considered to be excited is of the order of $\tau = \frac{h}{\Delta E}$ in which ΔE is the energy of interaction between the molecules. In a typical case this time may be in the range of 10^{-10} - 10^{-13} sec. This corresponds to an interaction energy of approximately 0.3 $cm.^{-1}$ - 300 $cm.^{-1}$. A composite molecule such as 2-phenylnaphthalene may be considered to be a crystal with two molecules. The magnitude of the interaction energy for such a system will generally be greater than that of molecules in crystals. Schnepp and Levy[67] have shown that energy transfer is very rapid between naphthalene and anthracene in the 9-anthryl-1'-naphthylalkane

---

[67] O. Schnepp and M. Levy, J. Am. Chem. Soc., 84, (1962), p. 172.

system. In this system the interaction energy ΔE is known to be small as evidenced by the fact that the absorption spectra of these compounds are essentially superpositions of the absorptions of the naphthalene and anthracene subsystems. Even in this weakly interacting non-planar system, only the anthracene emission was observed, when the naphthalene subsystem was excited by appropriately filtered radiation.

The absorption spectrum of 2-phenylnaphthalene cannot be considered a superposition of naphthalene and benzene absorptions. The absorption spectrum of 2-phenylnaphthalene is typical of that of a single hydrocarbon like naphthalene but some of the bands are severely red-shifted with respect to those of naphthalene. There are no transitions in the 2-phenylnaphthalene absorption spectrum that can be assigned to the benzene subsystem. One must conclude, therefore, that the interaction energy between the two subsystems of 2-phenylnaphthalene is much greater than that of the 9-anthryl-1'-naphthylalkane system. This indicates that the average time for excitation energy to remain in the benzene subsystem of 2-phenylnaphthalene must be shorter than the time for naphthalene excitation energy to remain in the naphthalene subsystem of the 9-anthryl-1'-naphthylalkanes.

Based on the experimental results on 2-phenylnaphthalene, it is obvious that the interaction energy between the phenyl and naphthyl rings will depend on the angle between the rings. The value of the interaction energy can be estimated in the two extreme cases in which the two rings are either co-planar or 90 degrees out of plane with respect to one another. In the case of planar 2-phenylnaphthalene

the interaction energy is estimated from the red-shift in the $^1L_b \leftarrow {}^1A$ transition to be approximately 2,500 cm.$^{-1}$ compared with that of naphthalene and in the 90 degree configuration the interaction energy must be at least 10 cm.$^{-1}$. If it is assumed that the benzene subsystem can be independently excited in the two extreme cases, then it is concluded that the average time for the excitation to remain on the benzene subsystem before the energy is transferred to the naphthalene subsystem is of the order of 1.3×10^{-14} sec. in the case of planar configuration and 3×10^{-12} sec. in the case of the 90 degree configuration. With energy transfer occurring in such short time intervals, one could not possibly expect to observe a benzene emission from 2-phenylnaphthalene, even if it were possible to independently excite the individual benzene subsystem.

There is at least one other situation that may arise in which it would be possible to observe two different emissions from 2-phenylnaphthalene. If by some means the phenyl ring of 2-phenylnaphthalene could be stabilized in the 90 degree out of plane configuration, the molecule should act essentially like an alkyl substituted naphthalene and should have an emission characteristic of the naphthalene subsystem. If, on the other hand, part of the molecules were distributed at some smaller equilibrium angle, at which there was appreciable resonance stabilization between rings, these molecules would have emission properties characteristic of a total 2-phenylnaphthalene molecule. If dual emissions of this kind were to be observed, they would in essence be emissions from two different molecular species,

not from a single molecule. The experimental evidence indicates that even this latter situation does not arise in 2-phenylnaphthalene but it may occur in some of the derivatives of 2-phenylnaphthalene in which the aromatic rings are stabilized in the 90 degree configuration.

Several derivatives of 2-phenylnaphthalene are observed to exhibit properties of a slightly perturbed naphthalene subsystem, when there is an appreciable distribution of 90 degree out of plane molecular configurations. These 90 degree configurations have $^1B_b \leftarrow {}^1A$ transitions in the 2200 - 2300 A. region reminescent of the 2-alkyl or 2-halonaphthalenes. The $^1B_b \leftarrow {}^1A$ transition of 2-phenylnaphthalene itself occurs at 2500 A., considerably red-shifted from that expected of a naphthalene absorption.

The $^1B_b \leftarrow {}^1A$ transitions indicate that 1-chloro-2-phenylnaphthalene and 1-bromo-2-phenylnaphthalene have appreciable populations of 90 degree configurations in the ground state at room temperature but not at 77°K. This is indicative of a stabilization of the 90 degree configuration in these compounds by an interaction between the large halogen atom and the benzene pi cloud. This interaction must be relatively small in the 1-halo-2-phenylnaphthalenes, since it does not occur at all in the case of 2-phenylnaphthalene and 1-fluoro-2-phenylnaphthalene and is not observed in the 1-chloro and 1-bromo derivatives at 77°K. The attraction between the 1-halogen and the 2'-hydrogen in the planar configuration apparently presents a much deeper minimum in the zero-point energy curve than the minimum at 90 degrees in the case of these compounds. The experimental obser-

vations lead to the conclusions that all the 1-halo-2-phenylnaphthalenes are planar or nearly planar in the equilibrium excited state. There is, therefore, little probability of observing an emission from an independent naphthalene subsystem of the 1-halo-2-phenylnaphthalenes.

In the 2'-halo-2-phenylnaphthalenes there appears to be little or no attraction between the 2'-halogen and 1-hydrogen to stabilize the planar configuration, and in the case of the 2'-chloro and 2'-bromo derivatives there is appreciable stabilization of the 90 degree configuration. In the absorption spectrum of 2'-chloro and 2'-bromo-2-phenylnaphthalene the characteristic naphthalene $^1B_b \leftarrow {}^1A$ transition is observed in the 2200 - 2300 A. region at room temperature and is observed to a lesser extent at 77°K. The transition is far more intense in the case of the 2'-bromo derivative than in that of the 2'-chloro derivative. Since this transition is observed with an appreciable intensity at 77°K, it must be concluded that the minimum in the zero-point energy curve at 90° is low enough to effectively compete with the second minimum at a smaller angle (not completely planar) created by the resonance stabilization between the two rings. From the relative intensities of the $^1B_b \leftarrow {}^1A$ transitions of the two configurations it is estimated that the minimum in the zero-point energy curve corresponding to the smaller angle is the deeper of the two and contains the greatest population of molecules. The data indicate that the geometry of the excited state is not greatly different from that of the major distribution in the ground state. This would indicate a possibility of two different molecular config-

urations in the excited state, especially in the case of 2'-bromo-2-phenylnaphthalene. This molecule provides the best change of any molecule studied to exhibit dual fluorescences; however, its fluorescence quantum yield is too low to permit observation of a second fluorescence.

Another molecule from which dual emissions might occur is 2'-methyl-2-phenylnaphthalene, which has a relatively intense $^1B_b \leftarrow {}^1A$ transition characteristic of a naphthalene system in the 90 degree configuration and another $^1B_b \leftarrow {}^1A$ transition characteristic of a slightly out of plane 2-phenylnaphthalene system. In this compound the $^1B_b \leftarrow {}^1A$ transition of the naphthalene subsystem essentially disappears at 77°K and there is some evidence that the planarity of the molecule is greater in the equilibrium excited state. It is, therefore, improbable that two emissions from 2'-methyl-2-phenylnaphthalene could be observed.

2-phenylnaphthalene itself shows no indication at all of having a $^1B_b \leftarrow {}^1A$ transition characteristic of a 90 degree configuration either at room temperature or 77°K. The $^1B_b \leftarrow {}^1A$ transition occurs at 2500 A. and is relatively narrow even at room temperature; this behavior suggests that there is a relatively narrow angular distribution of the molecules. The extinction coefficient of the $^1B_b \leftarrow {}^1A$ transition is appreciably higher than that of the compounds in which there was a distribution. The $^1C_b \leftarrow {}^1A$ transition in 2-phenylnaphthalene is very sharp with no noticeable shoulders on either side. It must be concluded that there is no measurable population of

90 degree configurations in 2-phenylnaphthalene at room temperature. Since there is indication that the planarity of 2-phenylnaphthalene is greater in the excited state, it is highly improbable to observe anything other than a total molecule fluorescence from 2-phenylnaphthalene.

The 6-bromo-2-phenylnaphthalene, 4'-chloro-2-phenylnaphthalene and 4'-bromo-2-phenylnaphthalene all appear to be similar to 2-phenylnaphthalene with respect to the absence of a $^1B_b \leftarrow {}^1A$ transition characteristic of the 90 degree configuration. There was some indication of increased ground state planarity of these compounds compared with that of 2-phenylnaphthalene. This reduces the probability of observing a second emission from these compounds.

Experimental evidence from phosphorescence lifetime measurements and quantum yields indicates that the phenyl ring also strongly interacts with the naphthalene ring in the triplet state. If the observed phosphorescence from 2-phenylnaphthalene were from a naphthalene chromophore, then one should observe little or no heavy atom effect from 4'-halogen substitution. There is observed a greater heavy atom effect in the 4'-position than in the 6-position. 2'-bromo-2-phenylnaphthalene would be expected to have the best chance of emitting a phosphorescence characteristic of naphthalene because of its higher probability of being 90 degrees out of plane. This molecule has an extraordinarily large degree of intersystem crossing presumably due to an external heavy atom effect from the 90 degree configuration. The spin-orbital coupling effect on phosphorescence lifetime is greatly

reduced, even less than that for the 4'-bromo derivative. This would indicate that the high degree of intersystem crossing is due to the 90 degree configuration of the excited singlet state, and that the triplet state corresponds to a more nearly planar configuration from which the external heavy atom effect is not observed.

In view of the experimental data presented, one must conclude that 2-phenylnaphthalene should be expected to exhibit only a single fluorescence and a single phosphorescence and that these emissions must be characteristic of a total molecule chromophore. The interaction of the phenyl ring does depend on the angle of rotation; however, the angle in 2-phenylnaphthalene itself apparently does not get large enough (90 degrees) to consider the molecule to be a naphthalene chromophore.

Since it has bee concluded that 2-phenylnaphthalene cannot be considered electronically simply as a combination of benzene and naphthalene subsystems, it must be considered as a molecular species with its own characteristic set of pi electron energy states. These energy states are somewhat unique in that they can vary greatly as the angle between the two aromatic rings varies. This has the effect of causing relatively large variations in transition energies with the substitution of simple alkyl or halo groups that are capable of changing the ring angle. Normally such substituents cause only minor energy changes when the substitution occurs along the axis of the transition.

2-phenylnaphthalene has the usual compliment of energy states typical of other hydrocarbon molecules like naphthalene and benzene in which the ^1L_b state is the lowest excited singlet state. The energy of the ^1L_b state of 2-phenylnaphthalene varies from approximately 31,450 $cm.^{-1}$ for the out of plane configuration to 29,240 $cm.^{-1}$ for the planar configuration. According to the SCFMO calculations this transition is polarized at an angle of 30.5 degrees with respect to the long axis of the naphthalene molecule. This corresponds approximately to an extension of a line drawn through the bond between the two rings. The $^1L_b \leftarrow {}^1A$ transition in 2-phenylnaphthalene is highly sensitive to substituents that are capable of changing the angle between the ring whether or not the substituents themselves are along the axis of polarization. Emission data indicates that the planar configuration is highly stabilized by polar resonance structures in the ^1L_b state. The molecule always has a strong tendency to become planar in the ^1L_b state, when it is not prevented from doing so by steric hindrance.

The ^1L_a state is the second excited energy level in 2-phenylnapthalene. This state varies from approximately 34,700 $cm.^{-1}$ in the case of the planar configuration to approximately 36,300 $cm.^{-1}$ in that of the out of plane configuration. The $^1L_a \leftarrow {}^1A$ transition is not as sensitive to changes in the ring angle as are the $^1L_b \leftarrow {}^1A$ and $^1B_b \leftarrow {}^1A$ transitions. According to the SCFMO calculations this transition is polarized at an angle of 36.3° with respect to the long axis of the naphthalene ring. The $^1L_a \leftarrow {}^1A$ transition in naphthalene is polarized

along the short axis, therefore the angle of 36.3° indicates that the $^1L_a \leftarrow {}^1A$ transition of 2-phenylnaphthalene is unique for this molecule and is not characteristic of the corresponding naphthalene transition.

The third excited energy level of 2-phenylnaphthalene is the ^1B_b state which varies from 40,000 $cm.^{-1}$ in the case of the planar configuration to approximately 44,400 $cm.^{-1}$ in that of the non-planar configuration. The $^1B_b \leftarrow {}^1A$ transition appears to be more sensitive to ring angle than is the $^1L_b \leftarrow {}^1A$ transition, however, this may be partly due to the difficulty in observing the $^1L_b \leftarrow {}^1A$ transition in the case of a 90 degree configuration because it is obscured by the more intense $^1L_a \leftarrow {}^1A$ transition. Changes in the energy of the $^1B_b \leftarrow {}^1A$ transition appear to be the best criterion for detecting changes in the angle between the ring planes. According to the SCFMO calculations on planar 2-phenylnaphthalene, the $^1B_b \leftarrow {}^1A$ transition is polarized at an angle of -26.2 degrees with respect to the long axis of naphthalene.

The highest energy state observable in 2-phenylnaphthalene in the near ultraviolet region is apparently the ^1C_b state. The energy of this state is approximately 47,170 $cm.^{-1}$ and apparently varies little with ring angle. The SCFMO calculations indicate that the $^1C_b \leftarrow {}^1A$ transition is polarized at an angle of -36.7° with respect to the naphthalene long axis.

The lowest triplet state of 2-phenylnaphthalene as observed in the phosphorescence spectrum is a typical ^3L_a state that occurs at approximately 20,500 $cm.^{-1}$. There is apparently little variation in the energy of this state with changes in ring angle.

The molar extinction coefficients for the 2-phenylnaphthalene transitions are observed to be 10^2, 10^4, 5×10^4 and 4×10^4 respectively for $^1L_b \leftarrow {}^1A$, $^1L_a \leftarrow {}^1A$, $^1B_b \leftarrow {}^1A$, and $^1C_b \leftarrow {}^1A$ respectively with some variations with ring angle. All these transitions are broad and structureless at room temperature, but a large increase in structure is observed at 77°K. The abnormally large increase in structure at low temperature is indicative of a Boltzmann distribution of molecular configurations about the angle between the rings. At 77°K only the lower energy angles are appreciably populated and the distribution is narrowed.

There are several additional research problems suggested by this research. The SCFMO calculations have been very successful in predicting the energy states in planar 2-phenylnaphthalene. These calculations should be extended to include the variations in energy with angular changes. If one could also obtain an experimental value for the ring angle in the equilibrium ground state from electron diffraction measurements and obtain a reasonable hydrogen-hydrogen repulsion function, it would be possible to calculate the shape of the ground state zero-point energy curve for 2-phenylnaphthalene. This could be compared with the curve qualitatively predicted from the experimental observations. A calculation of this kind would be similar to that carried out by Goodwin and Morton-Blake[68] on biphenyl.

---

[68] T. H. Goodwin and P A. Morton-Blake loc. cit.

It was observed that halogen substitution in the 4'-position has a relatively large spin-orbital coupling effect on 2-phenylnaphthalene. The experimental data indicate that 4'-halo-2-phenylnaphthalene molecules have relatively small angles between the rings. It would be very valuable to observe how spin-orbital coupling varies with 4'-halo substitution as the ring angle is changed. This could be accomplished by measuring phosphorescence lifetimes of compounds such as 2'-methyl-4'-chloro-2-phenylnaphthalene or 1-methyl-4'-chloro-2-phenylnaphthalene and the corresponding 4'-bromo derivatives. In these compounds the phenyl ring would be held at least partially out of plane by the methyl group. This experiment should essentially eliminate any possible effects of the 4'-halogen changing the planarity of the molecule compared with that of 2-phenylnaphthalene itself.

Since there was evidence that 2'-chloro and 2'-bromo had a stabilizing effect on the 90 degree molecular configuration, the next logical step is to attempt preparation of the 2'-iodo-2-phenylnaphthalene. This compound has a high probability of having predominantely 90 degree configuration and could not possibly become planar.

A final and very important experiment that is suggested is a temperature study of the $^1B_b \leftarrow {}^1A$ transitions for the compounds in which the 90 degree distribution was believed to be appreciably populated. This study should include a systematic study of the shape of the $^1B_b \leftarrow {}^1A$ transition distribution as the temperature varies to acertain whether or not it changes in accordance with a Boltzmann distribution. This should also allow one to calculate the energy

difference between the two minima in the zero-point energy curve. This experiment could also be extended to include 2-phenylnaphthalene and the fluoro derivatives in which no 90 degree distribution was observed. If raised to a high enough temperature, even these compounds should exhibit some population of the larger angles. One would expect little stabilization of the 90 degree configuration in these molecules due to the small size of the fluorine and hydrogen atoms.

These are only a few of the many experiments that can add to the knowledge about the nature of the 2-phenylnaphthalene system.

V

A SELECTED BIBLIOGRAPHY

1. Almenningen, A. and O. Bastiansen, "Electron-diffraction Studies on Biphenyl, 4,4'-bipyridine and 2,2'-bipyridine in the Gaseous State," Klg. Norske Videns Selsk. Skrifter, 4, (1958), p. 1-16.

2. Atoji, M. and W. N. Kipscomb, "The Structure of Hydrogen Fluoride," Acta. Cryst., 7, (1954), p. 173.

3. Baumik, M. L. and L. J. Nugent, "Time-resolved Spectroscopy of Europium Chelates," J. Chem. Phys., 43, (1965), p. 1680.

4. Bersohn, M. and J. C. Baird, An Introduction to Electron Paramagnetic Resonance, (New York: W. A. Benjamin, Inc. 1966), p. 96.

5. Bowen, E. J., "Fluorescence and Fluorescence Quenching," Quart. Rev., 1, (1947), p. 1-15.

6. Clar, E., "Absorption Spectra of Aromatic Hydrocarbons at Low Temperatures," Spectrochim. Acta, 4, (1950), p. 116.

7. Coffman, R. and D. S. McClure, "The Electronic Spectra of Crystalline Toluene, Dibenzyl, Diphenylmethane and Biphenyl in the Near Ultraviolet," Can. J. Chem., 36, (1958), p. 48.

8. Coulson, C. A. and J. Jacobs, "Conjugation Across a Single Bond," J. Chem. Soc. (1959), p. 2805

9. Coulson, C. A. and H. C. Longuet-Higgins, "The Interaction of two Conjugated Systems," Proc. Roy. Soc. (London), A195, (1948), p. 188.

10. Davydov, A. P., Theory of Molecular Excitons, (New York: McGraw-Hill Book Co., 1962), p. 146-160.

11. Ermolaev, V. L. and E. B. Sveshnikova, "Use of Triplet-Singlet Transfer for the Study of the Internal Degradation of Electronic Energy in Organic Molecules," Opt. Spectry., 16, (1964), p. 320.

12. Ferguson, J., "The Near-Ultraviolet Absorption Spectra of Naphthalene and its Monohalogen Derivatives in Solution," J. Chem. Soc. (1954), p. 304.

13. Förster, Th., Fluoreszenz Organischer Verbindungen, (Göttingen: Vanderhoeck und Ruprecht, 1951), Chapter IV.

14. Förster, Th., "Energy Transfer with Special Reference to Biological Systems," Disc. Faraday Soc., 27, (1959), p. 7.

15. Friedel, R. A., Milton Orchin and Leslie Reggel, "Steric Hindrance and Short Wavelength Bands in the Ultraviolet Spectra of Some Naphthalene and Diphenyl Derivatives," J. Am. Chem. Soc., 70, (1948), p. 199.

16. Goeppert-Mayer, M. and A. L. Sklar, "Calculations of the Lower Excited Levels of Benzene," J. Chem. Phys., 6, (1938), p. 645.

17. Goodwin, T. H. and D. A. Morton-Blake, "The Configuration of Diphenyl in the Crystalline and in the Vapor States: A Simple Non-bonded H-H Potential Function," Theoret. Chim. Acta. (Berl.), 1, (1963), p. 458.

18. Hargreaves, A. and S. H. Rizvi, "The Crystal and Molecular Structure of Biphenyl," Acta. Cryst., 15, (1962), p. 365.

19. Harris, James L., Spectroscopy of Composite Molecules Having Weakly Interacting Systems, Ph.D. Dissertation, Louisiana State University, Baton Rouge, (1965), p. 39.

20. Hey, D. H. and S. E. Lawton, "Synthesis of 2-Phenylnaphthalene," J. Chem. Soc., (1940), p. 378.

21. Hey, D. H. and E. W. Walker, "Union of Aryl Nuclei. Part VII. Reactions with Acyl Peroxides," J. Chem. Soc., (1948), p. 2217.

22. Hirshberg, Y. and R. N. Jones, "The Ultraviolet Absorption Spectra of Some Carboxy Derivatives of Naphthalene," Can. J. Res., 27, (1949), p. 437.

23. Hornig, D. F. and W. E. Osberg, "Infrared Spectrum and the Structure of the Low Temperature Phases of Crystalline HCl, HBr, and HI," J. Chem. Phys., 23, (1955), p. 662.

24. Jones, R. N., "Some Factors Influencing the Ultraviolet Absorption Spectra of Polynuclear Aromatic Compounds," J. Am. Chem. Soc., 67, (1945), p. 2127.

25. Kasha, M., "Collisional Perturbation of Spin-Orbital Coupling and the Mechanism of Fluorescence Quenching. A Visual Demonstration of Perturbation," J. Chem. Phys., 20, (1952), p. 71.

26. Kasha, M. and S. P. McGlynn, "Molecular Electronic Spectroscopy," Ann. Rev. Phys. Chem., 7, (1956), p. 403.

27. Kharasch, M. S. and R. L. Dannley, "The Thermal Decomposition of α and β-Dinaphthoyl Perioxides in Carbon Tetrachloride," J. Org. Chem., 10, (1945), p. 410.

28. Longuet-Higgins, H. C., and J. N. Murrell, "Electronic Spectra of Aromatic Molecules. V. Interaction of two Conjugated Systems," Proc. Phys. Soc. (London), A58, (1955), p. 601.

29. Lower, S. K. and M. A. El-Sayed, "The Triplet State and Molecular Electronic Processes in Organic Molecules," Chem. Rev., 66, (1966), p. 199.

30. Mataga, N. and K. Nishimoto, "Electronic Structure and Spectra of Nitrogen Heterocycles," Z. Physik. Chem., 13, (1957), p. 140.

31. McClure, D. S., "Electronic Spectra of Molecules and Ions in Crystals," Solid State Physics, 9, (1959), p. 3.

32. McClure, D. S., "Energy Transfer in Molecular Crystals and in Double Molecules," Can. J. Chem., 36, (1958), p. 59.

33. McClure, D. S., "Triplet-Singlet Transitions in Organic Molecules. Lifetime Measurements of the Triplet State," J. Chem. Phys., 17, (1949), p. 905.

34. McGlynn, S. P., "Energetics of Molecular Complexes," Chem. Rev., 58, (1958), p. 1113.

35. McGlynn, S. P., et. al., "External Heavy-atom Spin-orbital Coupling Effect. I. The Nature of the Interaction," J. Chem. Phys., 37, (1962), p. 1818.

36. McGlynn, S. P., et. al., "The External Heavy-atom Spin-orbital Coupling Effect. III. Phosphorescence Spectra and Lifetimes of Externally Perturbed Naphthalenes," J. Phys. Chem., 66, (1962), p. 2499.

37. Nurmukhametov, R. N. and G. V. Gobov, "The Luminescence Spectra of Fluorene," Opt. Spectry., 13, (1962), p. 384.

38. Ory, Horace, Effects of Electronic Excitation of Organic Molecules, Ph.D. Dissertation, Louisiana State University, Baton Rouge, (1957), p. 41.

39. Pariser, R. and R. G. Parr, "A Semi-empirical Theory of the Electronic Spectra and Electronic Structure of Complex Unsaturated Molecules," J. Chem. Phys., 21, (1953), p. 466.

40. Pariser, R., "Theory of the Electronic Spectra and Structure of Polyacenes and of Alternate Hydrocarbons," J. Chem. Phys., 24, (1956), p. 250.

41. Parker, C. A. and C. G. Hatchard, "The Possibilities of Phosphorescence Measurement in Chemical Analysis: Tests with a New Instrument," Analyst, 87, (1962), p. 664.

42. Pauling, L., The Nature of the Chemical Bond, (New York: Cornell University Press, 1948), p. 284-327.

43. Pauling, L., H. D. Sprinall, and K. J. Palmer, "The Electron Diffraction Investigation of Methylacetylene, Dimethylacetylene, Dimethyldiacetylene, Methylcyanide, Diacetylene and Cyanogen," J. Am. Chem. Soc., 61, (1939), p. 927.

44. Platt, J. R., "Classification of Spectra of Cata-condensed Hydrocarbons," J. Chem. Phys., 17, (1949), p. 484.

45. Plattner, P. A., "Konstitution Und Farbe der Azulene," Helv. Chim. Acta., 24, (1941), p. 283E.

46. Plattner, P. A., and E. Heilbronner, "Die Absorptionskurven des Azulens Und der fünf Monomethyl-azulene im Sichtbaren Bereich," Helv. Chim. Acta., 30, (1947), p. 910.

47. Plattner, P. A., and E. Heilbronner, "Die Ultraviolett-Absorptionsspektren der fünf Monomethyl-and einiger mehrfach substitutierten Azulene," Helv. Chim. Acta, 31, (1948), p. 804.

48. Pople, J. A., "A Theoretical Treatment of Excited States of Alternate Hydrocarbon Molecules Based on Self-Consistent Molecular Orbitals," Proc. Phys. Soc. (London), A68, (1955), p. 81.

49. Robertson, G. B., "Crystal and Molecular Structure of Biphenyl," Nature, 191, (1961), p. 593.

50. Robinson, G. W. and R. P. Frosch, "Electronic Excitation Transfer and Relaxation," J. Chem. Phys., 38, (1963), p. 1187.

51. Roy, J. K., "A Comparative Study of Singlet-Triplet Absorption in some Halogenated Toluenes in the Vapor and Liquid States," Indian J. Phys., 35, (1961), p. 143.

52. Schnepp, O. and M. Levy, "Intramolecular Energy Transfer in a Naphthalene-Anthracene System," J. Am. Chem. Soc., 84, (1962), p. 172.

53. Simpson, W. T., "Internal Dispersion Forces. The Polyenes," J. Am. Chem. Soc., 73, (1951), p. 5363.

54. Simpson, W. T., "Resonance Force Theory of Carotenoid Pigments," J. Am. Chem. Soc., 77, (1955), p. 6164.

55. Streitwieser, Andrew, Jr., Molecular Orbital Theory for Organic Chemists, (New York: John Wiley and Sons Inc., 1961), p. 33.

56. Syrkin, Y. K. and M. E. Dyatkina, Structure of Molecules and the Chemical Bond, (New York: Interscience Publishers Inc., 1950), p. 269-293.

57. Wharton, James H., Interpretations of the Electronic Energy States In Fluoranthene and Related Molecules, Ph.D. Dissertation, Louisiana State University, Baton Rouge, (1962), p. 1-4.

58. Williamson, L. H., The Effect of Low Temperature and Irradiation on the Electronic Spectra of the Conjugated Chelate System and Related Aromatic Compounds, Ph.D. Dissertation, Louisiana State University, Baton Rouge, (1965), p. 22.

59. Zanker, V. and W. Koerber, "Measurements of Fluorescence and Phosphorescence Yields and Lifetimes in Dihalogenated Acridines and Fluoresceins," Z. Angew. Phys., 14, (1962), p. 43.

VI

APPENDIX

A. Glossary of Abbreviations

1. A - Angstroms
2. ev - Electron volts
3. IP - Isopentane hydrocarbon solvent
4. 3-MP - 3-methylpentane hydrocarbon solvent
5. 3-MPIP - Mixed hydrocarbon solvent composed of 3-methylpentane and isopentane in a 1:6 volume ratio
6. mu - Millimicrons
7. SCFMO - Self consistent field molecular orbital

B. Spectra and Spectroscopic Data for Pure Fluoranthene

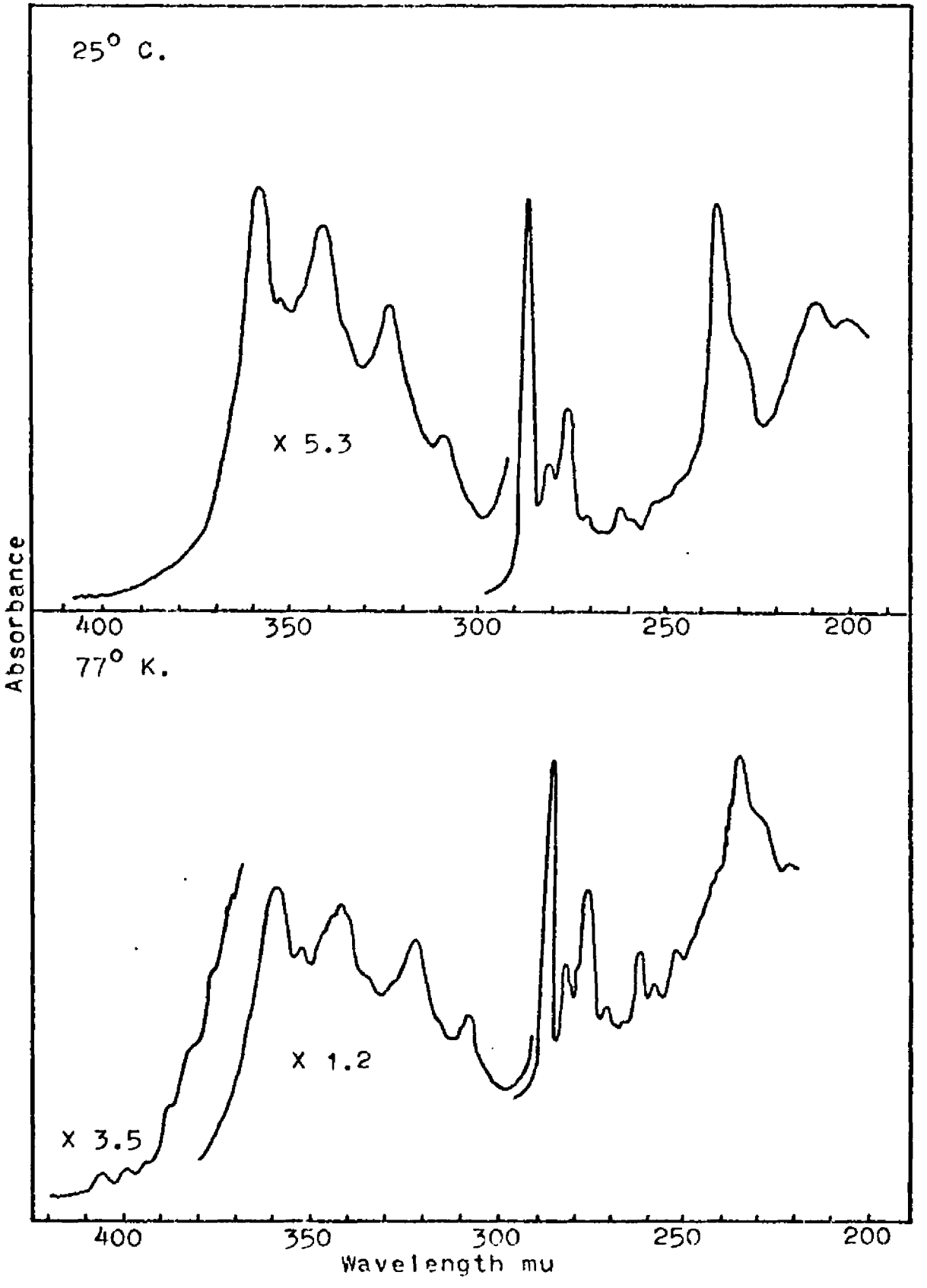


FIGURE 32. Room Temperature and 77° K. Absorption of Synthetic Fluoranthene In Hydrocarbon

TABLE XXXII

77°K Absorption Frequencies of Fluoranthene

A	Cm.$^{-1}$	$\Delta \nu$
4060	24,631	0
3990	25,063	432
3930	25,445	814
3875	25,806	1175
3820	26,178	1547
3770	26,525	1894
3720	26,882	2251
3600	27,778	0
3530	28,329	551
3425	29,197	1419
3370	29,673	1895
3230	30,960	3182
3190	31,347	3569
3090	32,362	4584
3050	32,787	5009
2930	34,130	6352
2880	34,722	0
2830	35,336	614
2820	35,461	739
2795	35,778	1056
2770	36,101	1379
2720	36,765	2043
2660	37,594	2872
2630	38,023	3301
2595	38,536	3814
2535	39,448	3726
2370	42,194	0
2300	43,478	1284

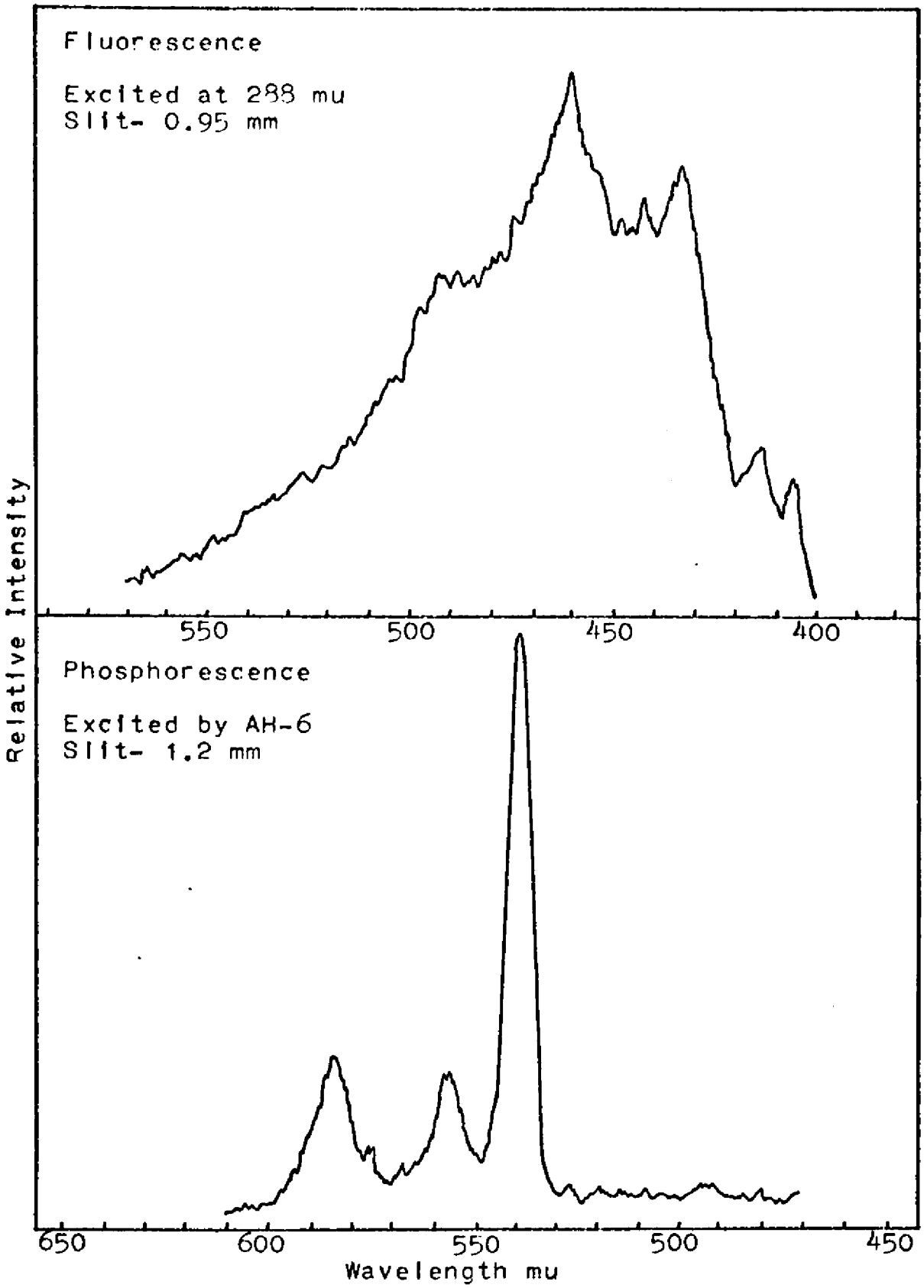


FIGURE 33. 77° K. Emission Spectra of Synthetic Fluoranthene in 3-methylpentane

TABLE XXXIII

Emission Frequencies of Fluoranthane

Fluorescence

A	Cm.$^{-1}$	$\Delta \nu$
4070	24,570	0
4150	24,096	474
4260	23,474	1096
4330	23,095	1475
4375	22,883	1687
4430	22,573	1997
4600	21,739	2831
4690	21,322	3248
4725	21,164	3406
4925	20,305	4265
5250	19,048	5522

Phosphorescence

A	Cm.$^{-1}$	$\Delta \nu$
5395	18,536	0
5520	18,116	420
5570	17,953	583
5605	17,841	695
5790	17,271	1265
5845	17,109	1427
5875	17,021	1515
5925	16,878	1658

VII

VITA

Homer Edward Holloway was born September 23, 1933, in Moss, West Virginia. He attended grade school in various cities throughout West Virginia. He attended Jr. high school and high school in Glenville, West Virginia. During his senior year he attended Springfield Township High School in Akron, Ohio, from which he graduated in 1952. He attended the University of Akron from 1952 to 1961, from which he received the Bachelor of Science degree in 1957 and the Master of Science degree in 1961. He was Assistant Professor of Chemistry at West Virginia Wesleyan College from 1961 to 1965.

In 1963 he entered the Graduate School of Louisiana State University. While studying at Louisiana State University, he was the recipient of a National Science Foundation Science Faculty Fellowship. He is now a candidate for the degree of Doctor of Philosophy.

He is married to the former Phyllis Armentrout of Burnsville, West Virginia and has two children, Teresa Ann, twelve and Stephen Edward, nine years old.

EXAMINATION AND THESIS REPORT

Candidate: Homer Edward Holloway

Major Field: Chemistry

Title of Thesis: Electronic Structure and Geometry of 2-Phenylnaphthalene Derivatives. A Study of the Electronic Transitions Observed in Absorption, Fluorescen and Phosphorescence Spectra.

Approved:

Robert V. Kaiman
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

May 10, 1967